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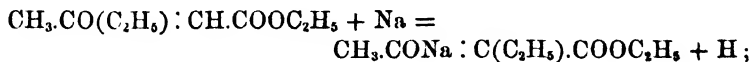
I.—Contributions to our Knowledge of Acetoacetic Ether.

By J. WILLIAM JAMES, Ph.D., F.C.S., University College of South Wales, Cardiff.

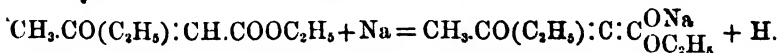
THE investigations of Geuther and Wedel have led them to ascribe the following constitutional formula to acetoacetic ether:—



In what way, however, the action of sodium on the monalkyl acetoacetic ethers takes place is not, according to this formula, at first sight apparent. By the action of sodium on ethylic ethylacetoacetate, for example, sodium ethylacetoacetic ether is produced. According to Geuther's views, there are two possible reactions which may take place here. In the first case, it may be thus formulated:—



or the action of sodium may alter the carboxyl-group. This would be expressed by the following equation:—



If the first reaction took place and the sodium ethylacetoacetic ether were acted on by acetic acid, one would not again obtain ethylacetoacetic ether, but a substance isomeric with it; in the second possibility, it could not be said with any certainty what sort of compound the action of acetic acid would give rise to.

I.—Action of dilute Acetic Acid on Sodium Ethylacetoacetic Ether.

The requisite ethylacetoacetic ether was prepared by Wislicenus' method (*Annalen*, 186, 183), viz., by the action of sodium and ethyl iodide on pure ethylic acetoacetate diluted with benzene. Ethyl bromide was tried in place of the iodide; it cannot however be recommended, as the reaction takes place exceedingly slowly.

By the action of sodium on ethylic ethylacetoacetate, Wislicenus (*Annalen*, 186, 189) says that considerable decomposition takes place, and that among the products *ethylic butyrate* is found, which is at once recognised by its characteristic odour. He also mentions that the sodium derivative of ethylic ethylacetoacetate is much more easily soluble than that of the ethylic acetoacetate itself. In consequence of this, it may be presumed that if *more* of the diluting liquid were used—instead of $\frac{3}{4}$ to 1 volume of benzene or ether, take say 3 or 4 volumes—a better result would be obtained, and very little decomposition take place, resulting in a higher percentage of the sodium derivative of the substituted ether, without the formation of ethylic butyrate and liquids of high boiling point. This is, as a matter of fact, the case.

Of the four experiments which I have made, ether was used three times, and benzene once, as the diluting liquid. The method of procedure was as follows:—

10 grams of pure ethylic ethylacetoacetate, boiling at 192—194°, were brought into a suitable flask, and diluted with 3 or 4 volumes of absolute ether or benzene. The theoretical quantity of sodium, 1·4 gram, was now introduced in small thin slices, cut under ether. The flask was connected with an inverted condenser by means of a Y-shaped tube which admits of the sodium being easily dropped in from time to time without sustaining any loss of the diluting liquid.

During the reaction, the liquid becomes slightly yellow, but there is not the slightest odour of ethylic butyrate. Nearly the whole quantity of sodium can be dissolved.

The product was now acidified with dilute acetic acid, and the oil which had separated out dried and fractionated. After two rectifications, 7 grams of a liquid which distilled at 192—194° were again obtained. The whole passed over below 200°, and after the ether had been boiled off the thermometer rose rapidly to 190°. The sp. gr. of the oil so obtained was 0·980 at 16°, whereas that of the ethylic ethylacetoacetate operated on was 0·981 at the same temperature.

In order to still further prove the identity of this product with the ethylic ethylacetoacetate used, and at the same time to see if it were possible by the use of more diluting liquid to obtain a better per-

centage than Wislicenus did, I converted it into ethylic diethylacetoacetate.

12 grams of the oil, obtained as above, diluted with 3 to 4 volumes of absolute ether, were operated on, and I ultimately obtained 6.5 grams of pure ethylic diethylacetoacetate, boiling at 210—212° (uncorr.), which is 55 per cent. of the theoretical quantity. Wislicenus (*Annalen*, 186, 191) obtained only 25 per cent., and his crude oil was always brown, whereas the above sample was colourless.

From these experiments, there can be scarcely any doubt that sodium ethylacetoacetic ether, when acted on with dilute acetic acid, is again converted into ethylic ethylacetoacetate.

II.—On certain mixed Di-allyl Acetoacetic Ethers.

Although a number of mixed di-substituted acetoacetic ethers have been prepared, we have no record as to whether the order in which these radicals are introduced is a matter of indifference or not, *i.e.*, whether the same bodies are produced or whether they are isomeric. In order to put this to the test, I chose first of all the radicals allyl and methyl, principally because allyl has not, so far, been used in a di-substituted ether.

1. Ethylic Allylmethylacetoacetate.

The ethylic allylacetoacetate (comp. Zeidler, *Annalen*, 187, 30) was prepared by the general method proposed by Conrad and Limpach (*Annalen*, 192, 153). Sodium was dissolved in absolute alcohol, ethylic acetoacetate added, and then allyl iodide; the mixture was warmed on a water-bath, the alcohol distilled off, and the residue treated with water until the sodium iodide was just dissolved, which caused the ether to float on the surface as an oil. The sodium iodide solution was now syphoned off, shaken with ether, this extract mixed with the oil, and the whole dried with calcium chloride. After rectifying, a quantity of ethylic allylacetoacetate was obtained, boiling at 198—205°. This substance was now converted into ethylic allylmethylacetoacetate by treatment with the required quantity of sodium and methyl iodide.

By the first distillation, nearly the whole quantity distilled at 210°, and after several rectifications the chief portion boiled at 209—211°, each time however a drop or two of a liquid of higher boiling point remained.

An analysis of the liquid boiling at 209—211° gave the following result :—

I. 0.3235 gram gave 0.2540 gram H_2O and 0.7515 gram CO_2 .
 II. 0.3190 ,, 0.2555 ,, ,, 0.7405 ,,

		Found.	
		I.	II.
C_{10}	Calculated. 65.2	63.3	63.3
H_{16}	8.7	8.7	8.8
O_3	26.1	—	—
<hr/>			
100.0			

Since ethylic allylmethylacetoacetate, $C_{10}H_{16}O_3$, contains more carbon than was found, it was probable that its boiling point lay somewhat higher. The liquid which had, during the fractionating, remained in the retort, was therefore submitted to distillation, in the hope of obtaining the purer compound, but without success, as the thermometer rose very rapidly from 210° to 360° , and a dark brown syrupy mass was left, which represented more than three-quarters of the whole liquid of high boiling point, only a drop or two having distilled between 210° and 360° .

This ethylic allylmethylacetoacetate has an exceedingly pleasant odour. It produces no coloration with ferric chloride, and is miscible in all proportions with alcohol, ether, and benzene.

2. *Ethylic Methylallylacetate.*

This substance was prepared in a manner precisely similar to the one just described, only with the difference that the methyl-group was first introduced and then the allyl.

I will only remark that when the ethylic methylacetoacetate is poured into the sodium ethylate solution, the mixture becomes solid from separation of white silky needles of the sodium derivative of this ether. On warming on the water-bath with addition of a little more alcohol, it may be dissolved, and the allyl iodide poured in.

On the first distillation I obtained, as in the previous case, a liquid boiling nearly all at 210° , which, after rectification, passed over for the most part at 209 — 211° , but each time a few drops of higher boiling liquid remained in the retort. An analysis gave the result:—

0.3055 gram gave 0.2400 gram H_2O and 0.7170 gram CO_2 .

	Calculated.	Found.
C ₁₀	65.2	63.9
H ₁₆	8.7	8.7
O ₃	26.1	—
	<hr/>	
	100.0	

The liquid of higher boiling point was also operated on as before, with a precisely similar result.

This ether has a very pleasant smell, and cannot be distinguished from the former substance in this respect. It gives no coloration with ferric chloride, and is soluble in all proportions in alcohol, ether, or benzene.

As I was unable to obtain either of these substances in the pure state, it cannot be said with certainty that ethylic allylmethyl- and methylallyl-acetoacetates are the same compound.

3. *Ethylic Methyleneacetoacetate.*

I now endeavoured to answer this question by using methyl and ethyl as the substituting radicals, and to this end prepared some ethylic methyleneacetoacetate by Conrad and Limpach's method. The compound finally obtained boiled very constantly between 195—196° (uncorr.).

4. *Ethylic Ethylmethyleneacetoacetate.*

Saur, who has already prepared this substance (*Annalen*, 188, 260), employed Wislicenus' method (*ibid.*, 186, 183 and 187). He gives its boiling point as "198° uncorrected," and also mentions that on the first distillation the chief quantity went over between 195° and 205°. As this boiling point did not correspond with that of the methylethyl ether which I had made, some ethylic ethylmethyleneacetoacetate was prepared by Conrad and Limpach's method. It boiled constantly between 195—196° (uncorr.), and by the first distillation all came over below 200°. Perhaps Saur's statement should read "198° corrected" instead of uncorrected.

Since the boiling points of ethylic ethylmethyl- and methylethyl-acetoacetates are identical, and their odour and action on ferric chloride is the same, it seems very probable that in mixed di-substituted acetoacetic ethers, the order of introducing the radicals is of no importance, and that the same compound is formed either the one way or the other.*

5. *Ethylic Acetylacetoacetate.†*

By the action of acetyl chloride on the product of the action

Even this, however, is not certain, as the ethylic methyleneacetoacetate prepared by Geuther (*Jenaische Zeitschrift*, 1865, 2, 403), boils at 186·8° (corr.), and the methylic ethyleneacetoacetate, which is isomeric with it, boils according to Brandes at 189·7° (corr.) (*Jenaische Zeitschrift*, 1865, 3, 33), these two substances having nearly the same boiling point.

† In the *Ber.*, 10, 733, is an abstract on "Acetylacetic ether," taken from a

of sodium on ethylic acetate, Lippmann only obtained ethylic acetoacetate (*Zeitschr. f. Chem.*, 1869, 29); neither could Wedel produce it from acetyl chloride and ethylic acetoacetate (*Annalen*, 219, 116), I have, however, succeeded in preparing it by the action of acetyl chloride on an ethereal solution of sodium acetoacetic ether. It appears, however, that H. Elion (*Rec. d. Trav. Chim. de Pays-Bas*, 2, 202—204; also *Ber.*, 16, 2762, under Diacetylessigäther) has recently prepared this body in a similar manner, and I therefore omit my work here, which will be found in the *Annalen*, 226, 210, in detail.

It is hardly necessary to mention that for the preparation of the derivatives of ethylic acetoacetate, which are intended to contain acid radicals, Conrad and Limpach's method is inapplicable by reason of the alcohol present.

It would, however, probably give a good result to make the sodium acetoacetic ether by using sodium ethylate, and remove the alcohol by distillation. A solution of the sodium salt in ether or benzene could then be acted on with the chloride of the required radical. In this manner I hope to succeed in preparing perfectly pure substances without resorting to distillation.

Metallic Derivatives of Ethylic Acetylacetoacetate.

Ethylic acetylacetoacetate has the property of a fairly strong acid; for instance, it is capable of expelling acetic acid from its salts, whereas ethylic acetoacetate, although giving rise to a series of "salts," is not able to do this.

Copper acetylacetoacetic ether may be prepared by simply shaking the ether in question with an aqueous solution of neutral copper acetate. 2 grams of ethylic acetylacetoacetate were shaken for some time in a small cylinder with a concentrated solution of copper acetate. The excess of the solution was filtered from the sky-blue crystalline salt which had formed, and this latter washed with water until the liquid passing through was no longer of a distinct blue colour.

On testing for copper with ammonia, a blue colour, although not very intense, is always obtained, a proof that the salt is not altogether insoluble in water.

It was now air-dried until constant in weight, and an analysis gave the following numbers :—

I. 0.2615 gram of light blue salt lost 0.0220 gram H_2O by stand-

paper by Demarçay in the *Compt. rend.*, 84. In this publication Demarçay calls acetoacetic ether "Ether acétyl acétique," and this has been erroneously translated into the *Berichte* as *Acetylacetic ether*.

ing over sulphuric acid, becoming dark blue in colour; heated at 100° the weight remained constant. After ignition in air 0.046 gram of CuO remained.

- II. 0.2730 gram substance lost 0.0225 gram H_2O over sulphuric acid, and 0.0485 gram CuO was obtained.
- III. 0.3210 gram salt, which had been heated to just 150° , whereby it melted to an emerald-green liquid, becoming dark blue and crystalline on cooling: after combustion, it gave 0.159 gram H_2O and 0.5530 gram CO_2 .

	Calculated for $(C_8H_{11}O_4)_2Cu + 2H_2O$.	Found.	
		I.	II.
Cu	14.3	14.0	14.2
$2H_2O$	8.2	8.4	8.2
	$(C_8H_{11}O_4)_2Cu$.	III.	
C	47.3	47.0	
H	5.4	5.5	

The hydrated salt is sky-blue, and loses its water completely over sulphuric acid, becoming deepened in colour to that of cobalt-blue. At 100° it is blue-grey, and again becomes dark blue on cooling. It melts at 148° to an emerald-green liquid, without suffering the least decomposition; at 128° it re-solidifies to a magnificent blue crystalline mass. If the "salt" be heated to 190 — 200° , a beautifully crystalline colourless substance sublimes, which has not yet been further investigated. The anhydrous salt is easily soluble in alcohol and ether, forming blue liquids; from these solutions it can be obtained in beautiful long silky dark blue needles; the alcoholic solution produces the finest crystals. It also readily dissolves in chloroform and benzene.

Nickel Acetylacetoacetic Ether.—If a nickel sulphate solution be shaken with a few drops of ethylic acetylacetoacetate, with addition of a drop or two of sodium hydroxide, a precipitate is obtained, which is crystalline and of a light green colour. A sample of the salt was air-dried, and the nickel estimated with this result:—

0.2605 gram substance gave, after ignition, 0.440 gram nickel oxide.

Ni...	Calculated for—		Found.
	$(C_8H_{11}O_4)_2Ni$.	$(C_8H_{11}O_4)_2Ni + 2H_2O$.	
...	14.5	13.3 per cent.	13.24 per cent.

There was not a sufficient quantity of substance left to confirm the percentage of water.

Cobalt sulphate gives the same result as with nickel; the precipitate is rose-red.

Lead and zinc acetates produce no insoluble salts.

The strongly acid nature of ethylic acetylacetoacetate, which is manifested by the formation of its copper salt in the simple manner just described, may be employed on account of the comparatively feeble acid nature of ethylic acetoacetate, for the separation, and often very conveniently for the detection, of these two ethers, by converting them into their copper compounds. It is only necessary to shake a mixture of the two ethers with neutral copper acetate solution, when *blue* copper acetylacetoacetic ether separates out, and after filtering it off, to add a few drops of sodium hydroxide solution to the filtrate, which causes *pale-green* copper acetoacetic ether to form. For this purpose, that portion of the distillate boiling below 200° , which is obtained in preparing the acetyl compound, may be used with great advantage.

Decomposition of Ethylic Acetylacetoacetate by Water at the Ordinary Temperature.

This reaction has also been given by H. Elion (*Rec. Trav. Chim.*, July, 1884), and I can substantiate his observations in every way, viz., that ethylic acetylacetoacetate is decomposed into ethylic acetoacetate and acetic acid. For details see *Annalen*, 226, 215.

Action of Sodium Ethylate on Ethylic Acetylacetoacetate.

I hoped by the action of sodium ethylate on ethylic acetylacetoacetate to produce its sodium compound, and then with methyl iodide to obtain the methyl-derivative, but, on carrying out the experiment, I got a liquid which, after fractional distillation, went over constantly between $179-180^{\circ}$ (uncorr.), whereas a liquid boiling higher than this was only present in small quantity. This substance boiled at the same temperature as ethylic methylacetoacetate, and an analysis proved that it consisted of this body:—

0.2610 gram gave 0.1960 gram H_2O and 0.5560 gram CO_2 .

	Calculated for ethylic methylacetoacetate.	Found.
C	58.3	58.1
H	8.3	8.3

If the action of the sodium ethylate on the acetyl compound took place in such a way that acetyl and sodium changed places, ethylic acetate would certainly be formed, and, in order to put this to the test, I made the following experiment:—

0.4 gram of sodium was dissolved in 4 c.c. of absolute alcohol, and 3 grams of pure ethylic acetylacetoacetate were poured in. Reaction

began at once, the mixture becoming hot, and a strong smell of ethylic acetate was produced. The alcohol was now distilled off on the water-bath and tested carefully for ethylic acetate by distilling it twice to half its volume, and treating that portion which passed over first after the third distillation with a concentrated solution of calcium chloride, which caused the ethylic acetate to separate on the surface as an oily layer.

The residue which remained in the distilling apparatus, after removing the alcohol, was acidified with dilute acetic acid and the separated oil taken up with ether. After drying and evaporating this, the remainder, weighing 2.5 grams, was distilled. It boiled at 120—200°, and after three rectifications a liquid was obtained which passed over at 175—180°; this was shown to be *ethylic acetoacetate* by converting it into its *green* copper salt. The other portion, about one-third, was easily proved to be undecomposed ethylic acetylacetoacetate by making the *blue* copper salt without the aid of sodium hydroxide.

From this experiment, it is clear that the alkyl-derivatives of ethylic acetylacetoacetate cannot be prepared by the above method, since the latter is decomposed by the alcoholate as shown by the following equation:—



6. *Ethylic Methylacetylacetoacetate.*

This compound was prepared from ethylic methylacetoacetate in a similar manner to ethylic acetylacetoacetate. On distilling, nearly the whole of the oil passed over between 190—220°, and from this I separated, on the third distillation, two portions boiling at 205—215° and 215—220°. I could not succeed in obtaining any constant boiling point, and after each distillation rather a large quantity of dark-brown resinous matter remained, substances of lower boiling points being at the same time produced.

The above liquids were analysed with this result:—

- I. 0.2755 gram gave 0.1990 gram H₂O and 0.5795 gram CO₂.
 II. 0.3075 „ 0.2195 „ „ 0.6495 „

Calculated for ethylic methylacetylacetoacetate.		Found.	
		I. 205—215°.	II. 215—220°.
C ₈	58.1	57.34	57.6
H ₁₄	7.5	8.0	7.9
O ₄	34.4	—	—
<hr/>			
100.0			

Ethyllic methylacetylacetoacetate is a colourless, mobile, pleasant-smelling liquid, which is decomposed by distillation in the same way as ethyllic acetylacetoacetate but in a greater degree. It gives a fine raspberry-red coloration with ferric chloride, which is similar to that formed by the acetyl compound. Blue litmus-paper is not reddened unless water is added. It dissolves in alcohol, ether, or benzene, but only slightly in water.

With copper acetate, it gives no precipitate, neither is one formed on adding dilute sodium hydroxide; therefore this ethyllic methylacetylacetoacetate forms no (insoluble) copper salt. It appears to be only partially decomposed by water.

7. Ethyllic Benzoylacetoacetate.

This substance has already been prepared by Bonné (*Annalen*, 187, 1), and I would only remark, that if the benzoyl chloride is diluted with 2 volumes of ether, cooling with ice is quite unnecessary.

Ethyllic benzoylacetoacetate also has the properties of a fairly strong acid, and is capable of displacing acetic acid.

Copper Benzoylacetoacetic Ether.—1 gram of the ether, which smelt slightly of benzoyl chloride, was well shaken with neutral copper acetate solution until the blue oily bead, which was first of all produced, was converted into a dirty green crystalline salt. This was filtered off, washed with cold water, and then air-dried until constant in weight.

On analysing the substance I obtained the following numbers:—

0.2550 gram lost 0.0150 gram H_2O on heating at 100° , and left 0.0400 gram CuO .

Calculated for (C ₁₃ H ₁₄ O ₄) ₂ Cu + 2H ₂ O.		Found.
Cu	11.2	12.5
2H ₂ O	6.4	5.9

As this analysis did not agree with the calculated numbers as well as was expected, I thought the salt was probably mixed with a little copper benzoate which contains some 20 per cent. of copper and no water.

Two crystallisations from absolute alcohol were sufficient to remove a salt which proved to be copper benzoate, it being only sparingly soluble in this liquid. Unfortunately there was not sufficient of the substance which crystallised from the alcoholic solution in dark-blue needles for another analysis.

Since the presence of copper benzoate could only have arisen from the benzoyl compound containing a little benzoyl chloride, the original

product was warmed with absolute alcohol and allowed to remain for 24 hours in order to destroy the influence of the latter by converting it into ethyl benzoate. After this water was added, and some of the separated oil vigorously shaken as before; but this time I could not succeed in breaking the blue oily bead; the mixture was therefore rubbed in a mortar for some time, washed with water, pressed between filter-paper, and dissolved in benzene. In the fine blue crystalline substance which had separated out the copper was determined after removing the benzene by heating at 100°.

0.1750 gram substance after ignition gave 0.0260 gram CuO.

	Calculated for (C ₁₃ H ₁₃ O ₄) ₂ Cu.	Found.
Cu	11.9 per cent.	11.8 per cent.

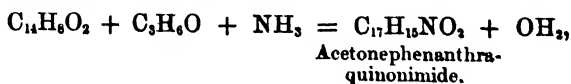
Copper benzoylacetoacetic ether is light blue in the hydrated state, but becomes a little darker if anhydrous. It melts with decomposition between 180—190°. It dissolves in alcohol, benzene, or ether, but not very easily in the first two solvents: from all three it may be obtained in the crystalline form.

II.—On Additive and Condensation Compounds of Diketones with Ketones.

By FRANCIS R. JAPP, M.A., Ph.D., and N. H. J. MILLER, Ph.D.

Introduction.

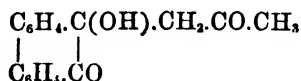
IN a former communication by Japp and Streatfeild (this Journal, 1882, Trans., 270), it was shown that phenanthraquinone, acetone, and ammonia react according to the equation—



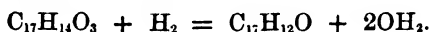
and that, when the compound thus obtained is treated with aqueous acids, it takes up water and parts with ammonia, yielding a compound of the formula C₁₇H₁₄O₃; this contains the elements of acetone and phenanthraquinone, and may, in fact, be obtained in small quantity by heating these two substances together. It may therefore receive, the name *acetonephenanthraquinone*. Owing to the ease with which, on heating, it was decomposed into acetone and phenanthraquinone, a

constitutional formula was assigned to it, in which the union of the two molecules of the generating compounds was represented as taking place by means of the oxygen-atoms.

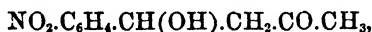
A further study of the reactions of this compound has now shown that it possesses the constitution—



Thus when reduced with zinc-dust in acetic acid solution, it yields a compound of the formula $\text{C}_{17}\text{H}_{12}\text{O}$:—

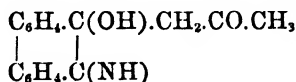


As the carbon residues of the acetone and phenanthraquinone molecules do not part company during this reaction, it is highly improbable that they could have been united merely through the medium of the oxygen-atoms. The chief argument, however, in favour of the constitutional formula above given is to be found in the analogy to several similar compounds to be described in the present communication. Owing to the greater ease with which these compounds can be obtained, their reactions have been more thoroughly studied. The above formula is also in keeping with the analogy to the additive compound of orthonitrobenzaldehyde with acetone—



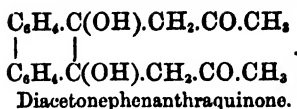
since obtained by Baeyer and Drewsen (*Ber.* 15, 2858).

The most probable formula for acetonephenanthraquinonimide appears to be—



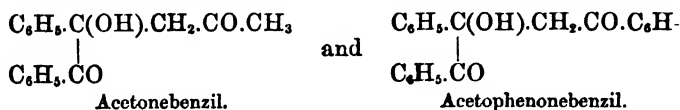
That the imido-group attaches itself to the phenanthraquinone residue, and not to the acetone residue, is rendered probable by the results which we have obtained by acting with potash solution on a mixture of phenanthraquinone and acetone. In this case no imidogen can replace the oxygen of one carbonyl-group of the phenanthraquinone: under the influence of the potash, therefore, both carbonyl-groups take part in the reaction, and an additive compound of one molecule of phenanthraquinone with *two* molecules of acetone is obtained. To this compound we assign the formula—

* This formula was first suggested by Dr. Armstrong during the discussion which followed the reading of the above-mentioned paper, but was rejected at the time by the authors of the paper.

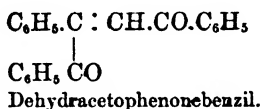


Under other conditions, we obtain an additive compound of 2 mols. of phenanthraquinone with 1 mol. of acetone. We also describe condensation compounds obtained from the above additive compounds by the elimination of the elements of water.

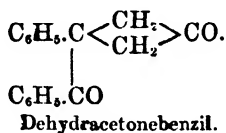
In order to extend the application of these reactions, we have studied the action of potash on mixtures of benzil with acetone and with acetophenone respectively, and have obtained the compounds—



The compound obtained from acetonebenzil by the abstraction of water has considerable theoretical interest. Whereas acetophenonebenzil parts with its hydroxyl-group along with a hydrogen-atom from the contiguous methylene-group to yield an unsaturated compound of the formula—



in the case of acetonebenzil the hydroxyl-group appears to be eliminated along with a hydrogen-atom from the methyl-group, so as to form a closed chain compound of the formula—



The evidence in favour of these views will be given in detail in the present paper.

1. PHENANTHRAQUINONE AND ACETONE.

a. *Action of a Small Quantity of Potash on a Mixture of Phenanthraquinone and Acetone.*

50 grams of very finely powdered phenanthraquinone were introduced into a small flask along with 43 grams of pure acetone* (i.e., in

* Many of the reactions described in this paper yield no trace of the desired

the proportion of 1 mol. of the quinone to 3 mols. of acetone) and 2 c.c. of a strong solution of potash (sp. gr. 1.27) were then added. On shaking the flask, a reaction took place attended with considerable rise of temperature: the phenanthraquinone dissolved, and the liquid became dark-coloured. After standing over night, the whole had solidified to a yellowish-brown mass. This was broken up, then triturated with ether until completely disintegrated, poured upon a filter, and washed with ether until the liquid ran through only slightly coloured. The treatment of the filtrate will be described later on. The crude substance was thus obtained as a yellowish powder.

The first ethereal washings from the above process were almost black, and, as it seemed therefore that the strong potash had exercised a prejudicial influence, experiments were made to ascertain whether, by employing a more dilute solution of potash, a purer product could not be obtained. It was found that, under these conditions, far less heat was evolved, the solution retained its pale colour, and the quinone, without dissolving, was transformed into an almost white powder. These favourable appearances were, however, entirely deceptive. The white powder, on treatment with solvents, proved to be merely phenanthraquinone superficially coated with the new compound. In order that a complete transformation of the quinone may take place, there must be complete solution, and this, as far as our experiments go, is best effected as above by the use of strong potash, and at the expense of a portion of the material.

The yellowish powder was dissolved in boiling acetone, in which it is sparingly soluble. From the acetone solution, it was deposited, by spontaneous evaporation,* in well-formed short oblique prisms, which, after recrystallising two or three times, were quite colourless.

The new substance is sparingly soluble in the ordinary organic solvents. Glacial acetic acid and amyl alcohol dissolve it most readily, but by boiling with these solvents it is speedily decomposed. Acetone and benzene were found to be the most suitable solvents.

products unless pure acetone is employed, and for this purpose a purification by means of the bisulphite compound is necessary. In the case of one of these reactions, which with acetone from the bisulphite compound gave excellent results, we attempted to employ a sample of acetone which had been repeatedly fractioned with a Le Bel-Henninger apparatus, and showed a constant boiling point; but hardly any of the compound was obtained. We may remark that various bought specimens of acetone, ostensibly prepared "from the bisulphite compound," utterly failed to stand the test of these reactions, and yielded only resinous products from which nothing definite could be extracted.

* In a short preliminary notice of this reaction, forwarded to Berlin in English, and published in the *Berichte* (16, 282), the words of the English manuscript "by spontaneous evaporation" were transformed by the Berlin translator into "unter freiwilliger Erwärmung" ("with spontaneous rise of temperature").

The melting point cannot safely be employed as a criterion of purity. When heated, the compound turns yellow between 150° and 160°, and melts at 187°, at the same time giving off acetone. The substance which remains behind is impure phenanthraquinone.

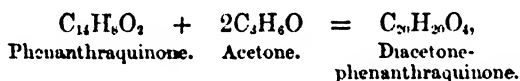
Analysis gave numbers agreeing with the formula $C_{20}H_{20}O_4$:—

	Substance.	CO ₂ .	OH ₂ .
I	0.1594	0.4321	0.0930
II	0.1550	0.4212	0.0908
III	0.1713	0.4637	0.0978

	Calculated for $C_{20}H_{20}O_4$.		Found.		
			I.	II.	III.
C ₂₀	240	74.07	73.93	74.11	73.82
H ₂₀	20	6.18	6.47	6.50	6.34
O ₄	64	19.75	—	—	—
	324	100.00			

Analyses I and II were made with one preparation; in III a second preparation was employed.

The compound has been formed according to the equation—



and we assign to it the constitution expressed by the formula already given on p. 13. In accordance with the system of nomenclature adopted by us for these compounds, it would receive the name *diacetonephenanthraquinone*.

Action of Acetic Anhydride on Diacetonephenanthraquinone.—A few grams of the compound were boiled with acetic anhydride. No more anhydride than is sufficient for solution ought to be employed, and the boiling should be discontinued as soon as everything has dissolved, otherwise only a red resin is obtained. On cooling the liquid—an operation which ought to be performed rapidly—white crystals were deposited; these were washed with ether and recrystallised from boiling benzene. The new substance was thus obtained in colourless pointed prisms, melting at 179—181°.

A further quantity of less pure substance can be separated from the acetic anhydride mother-liquor by shaking it with water; but if alcohol is employed to destroy the excess of anhydride, nothing but the red resin is obtained.

The colourless compound gave the following results on analysis :—

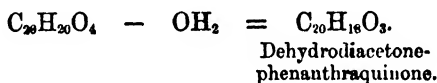
	Substance.	CO ₂ .	OH ₂ .
I.....	0.1478	0.4232	0.0840
II.....	0.1174	0.3365	0.0628

These numbers lead to the formula C₂₀H₁₈O₃ :—

	Calculated for C ₂₀ H ₁₈ O ₃ .		Found.	
			I.	II.
C ₂₀	240	78.43	78.13	78.18
H ₁₈	18	5.88	6.31	5.94
O ₃	48	15.69	—	—
	306	100.00		

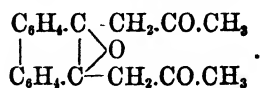
Different preparations were used in these analyses.

The compound is therefore formed from diacetonephenanthraquinone by the elimination of a molecule of water, and may be named *dehydrodiacetonephenanthraquinone* :—



There are various ways in which a molecule of water might be removed from a compound of the constitution of diacetonephenanthraquinone: our experiments do not enable us to decide between these. We could not succeed in preparing an additive compound with bromine.

Taking into consideration the fact that monacetonephenanthraquinone does not part with water when treated with acetic anhydride, it seems the most probable view that in the foregoing case the dehydration takes place between two hydroxyl-groups. Regarding diacetonephenanthraquinone as a glycol, the compound obtained by dehydration would thus be an analogue of ethylenic oxide :—



Formation of Monacetonephenanthraquinone.—The dark-coloured ethereal washings obtained in the preparation of diacetonephenanthraquinone were decolorised by shaking with freshly ignited animal charcoal. On spontaneous evaporation, the solution deposited colourless crystals of monacetonephenanthraquinone, recognisable by its melting point (90°), and its characteristic crystalline form.

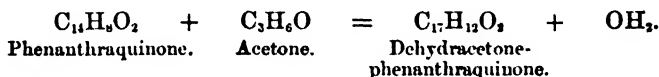
b. *Action of an Excess of Potash on a Mixture of Phenanthraquinone and Acetone.*

If an excess of the potash solution (sp. gr. 1·27) is employed in this reaction, the yield of diacetonephenanthraquinone is not so good, and the ethereal washings contain a new substance. The quantity of the latter was small; but sufficient was obtained for analysis. It was crystallised several times from boiling benzene until a constant melting point was obtained. It is deposited from the benzene solution in groups of small colourless needles, which under the microscope appear as long pointed prisms. It is moderately soluble in hot benzene or alcohol; almost insoluble in these liquids in the cold. Ether dissolves it rather readily. It melts at 195° without evolving gas.

Analysis gave figures leading to the formula $C_{17}H_{12}O_2$:—

	Substance.	CO ₂ .	OH ₂ .
I	0·1310	0·3946	0·0591
	Calculated for $C_{17}H_{12}O_2$.		Found.
C ₁₇	204	82·25	82·15
H ₁₂	12	4·85	5·01
O ₂	32	12·90	—
	<hr/> 248	<hr/> 100·00	

The compound is a condensation-product of phenanthraquinone and acetone, and we therefore propose to name it *dehydracetonephenanthraquinone* :—



It is probably formed from monacetonephenanthraquinone by elimination of a molecule of water. The corresponding transformation in the case of monacetonebenzil is described later on.

The difficulty of obtaining this substance in any quantity precluded a study of its reactions. Its constitution, however, is probably analogous to that of the corresponding condensation-product of benzil and acetone (*q.v.*).

c. *Acetonephenanthraquinone.*

In order to study the reactions of this compound, a quantity of it was prepared from acetonephenanthraquinonimide by a method mentioned by Japp and Streatfeild (*Trans.*, 1882, 273), but not

further worked out by them. This method consists in the decomposition of the latter compound with an aqueous solution of oxalic acid. The following mode of applying the reaction was found to give satisfactory results: 50 grams of phenanthraquinone were shaken in a flask with 60 grams of acetone and 40 c.c. of strong aqueous ammonia, and the acetonephenanthraquinonimide thus formed was filtered off and washed with ether as described in the above-mentioned paper. Without getting rid of the adhering ether, the crude compound was suspended in water, and the resulting thick cream poured, with constant stirring, into a solution of 90 grams of crystallised oxalic acid in 800 grams of water (temperature about 25°). Almost everything dissolved; but in a short time the liquid became turbid, and the separation of minute needles of acetonephenanthraquinone commenced. After standing for two days, the compound was separated by filtration, and thoroughly washed with cold water in order to remove any oxalic acid. It was then dried by exposure to the air, and dissolved in ether. By spontaneous evaporation of the ethereal solution, the compound was obtained in large lustrous prismatic crystals. The last ethereal mother-liquors, which are rather dark, may be decolourised by shaking with freshly ignited animal charcoal. From 50 grams of phenanthraquinone, 37 grams of a pure product were obtained.

Action of Nascent Hydrogen on Acetonephenanthraquinone.—A quantity of the above compound was dissolved in cold glacial acetic acid, and zinc-dust was added in small quantities from time to time, keeping the flask in cold water. After a few days, the whole was poured into water to precipitate the substance and dissolve zinc acetate. The substance was then collected along with the excess of zinc-dust, dried at ordinary temperatures, and extracted from the zinc-dust with ether, in which it is very soluble. The impure substance, remaining after evaporation of the ether, was crystallised from hot alcohol, which removed a quantity of very soluble red gum. It was deposited from the alcoholic solution in long slender needles, which, on recrystallisation from the same solvent, melted constantly at 121°. The compound is soluble in almost all proportions in ether and chloroform, readily soluble in boiling alcohol, almost insoluble in cold alcohol. It sublimes without decomposition in feathery crystals. The yield of substance is small.

Analysis gave the following results:—

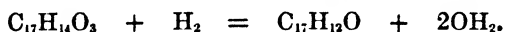
	Substance.	CO ₂ .	OH ₂ .
I.....	0.0986	0.3168	0.0488
II.....	0.1120	0.3601	0.0545

These numbers lead to the formula C₁₇H₁₂O.

	Calculated for $C_{17}H_{12}O$.		Found.	
	I.	II.	I.	II.
C_{17}	204	87·93	87·62	87·68
H_{12}	12	5·17	5·49	5·40
O	16	6·90	—	—
	232	100·00		

These analyses were made with different preparations of substance.

In the formation of this compound, 1 mol. of acetonephenanthraquinone takes up 1 mol. of hydrogen and parts with 2 mols. of water:—



When bromine is added to a solution of the substance in chloroform, the colour of the bromine instantly disappears, and a bromine-derivative—probably additive—separates in slender needles. The quantity obtained was not sufficient for analysis, and the preparation of a larger quantity would have involved the sacrifice of more phenanthraquinone than we could conveniently spare.

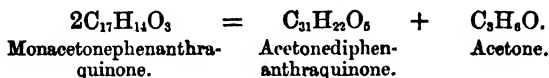
Action of Dilute Potash on Monacetonephenanthraquinone in Alcoholic Solution.—A few drops of dilute aqueous potash were added to a cold alcoholic solution of monacetonephenanthraquinone. The liquid at once assumed a yellow colour, and minute crystals adhering to the sides of the vessel soon began to form. The separation of crystals was complete in about 24 hours, when the liquid was poured off, and the crystals, which were yellow, were washed with alcohol, dried, and recrystallised from boiling benzene until they were colourless. Thus obtained, the substance forms minute rhomboidal crystals which, when heated, turn yellow at 150–160°, and melt at 190°, evolving gas and leaving an orange-coloured residue of phenanthraquinone. It is very sparingly soluble in all the usual solvents, and is deposited from its benzene solution only after long standing.

Analysis gave figures agreeing with the formula $C_{31}H_{22}O_5$:—

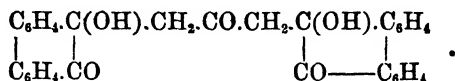
	Substance.	CO_2 .	OH_2 .
I.	0·1344	0·3858	0·0617
• II.	0·1054	0·3020	0·0456

	Calculated for $C_{31}H_{22}O_5$.		Found.	
	I.	II.	I.	II.
C_{31}	372	78·48	78·28	78·14
H_{22}	22	4·63	4·80	4·80
O_5	80	16·89	—	—
	474	100·00		

The formation of this compound may be expressed thus :—



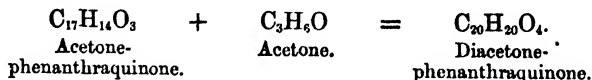
It thus contains the elements of 1 mol. of acetone with 2 mols. of phenanthraquinone, and may receive the name *acetonediphenanthraquinone*. Judging from analogy, it most probably possesses the constitution—



There are thus three distinct compounds containing the elements of phenanthraquinone and acetone in different proportions :—

Acetone.		Phenanthraquinone.		Resulting compound.
1 mol.	+	1 mol.	=	$\text{C}_{17}\text{H}_{14}\text{O}_3$ (Acetonephenanthraquinone).
2 „	+	1 „	=	$\text{C}_{20}\text{H}_{20}\text{O}_4$ (Diacetonephenanthraquinone).
1 „	+	2 „	=	$\text{C}_{31}\text{H}_{22}\text{O}_5$ (Acetonediphenanthraquinone).

Action of Strong Potash on a Solution of Acetonephenanthraquinone in Acetone.—On adding an excess of strong potash (sp. gr. 1·27) to a cold concentrated solution of acetonephenanthraquinone in acetone, the liquid became dark, and considerable heat was liberated. On cooling, the liquid layer floating on the surface of the potash solidified, and on washing the substance with ether and recrystallising it from acetone, the characteristic crystals of diacetonephenanthraquinone were obtained, melting at 187°. The following reaction had therefore occurred :—



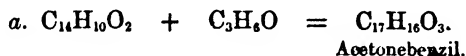
Action of Amines on Acetonephenanthraquinone.—It had already been shown (*loc. cit.*) that by the action of ammonia on acetonephenanthraquinone, one oxygen-atom of this compound could be replaced by imidogen. We, therefore, determined to study the action of amines. The reaction was allowed to take place in the cold in ethereal solution. With *ethylamine*, nothing but a green gummy mass was obtained which turned blue when treated with hydrochloric acid. With *diethylamine*, crystals were gradually deposited from the

ethereal solution. These proved to be acetonediphenanthraquinone; so that the action of diethylamine was identical with that of potash. With *aniline*, the substance yielded nothing but a green, gummy mass.

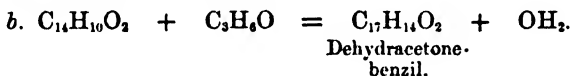
2. BENZIL AND ACETONE.

By the action of an aqueous solution of potash on a mixture of benzil and acetone, three distinct products may be obtained according to the conditions of the experiment.

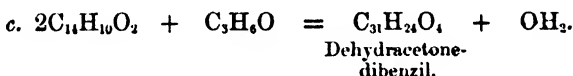
a. By acting with a small quantity of potash on benzil dissolved in an excess of acetone, the additive compound *acetonebenzil* is formed:—



b. By employing an excess of potash under conditions otherwise the same as the foregoing, a condensation-product of 1 mol. of benzil with 1 mol. of acetone is obtained:—



c. By acting with a small quantity of potash on acetone mixed with an excess of benzil, a condensation-product of 2 mols. of benzil with 1 mol. of acetone is formed:—



a. Action of a small Quantity of Potash on a Mixture of Benzil with Excess of Acetone.

50 grams of finely powdered benzil are introduced into a flask along with 30 grams of acetone,* and $\frac{1}{4}$ c.c. of strong potash (sp. gr. 1.27) is added. The flask is then corked, after which the whole is shaken until the benzil has entirely dissolved, about an hour being required for this operation. The liquid at the same time assumes a reddish colour. If, after standing for two or three days there is no sign of crystallisation, a drop of the liquid should be removed, allowed to solidify by exposure to the air, and the crystalline substance thus obtained added to the contents of the flask. The whole is again allowed to stand as long as the separation of crystals con-

* The employment of an acetone purified by means of the bisulphite compound is in this reaction *indispensable*—not merely for obtaining a good yield of the compound, but in order to obtain any of the compound at all (see note, p. 13).

tinues, a process which is generally complete in about a week. Before pouring off the still liquid portion from the crystals, it is advantageous, especially in warm weather, to allow the flask to remain for some time in a refrigerator. On the other hand, the aid of the refrigerator must not be called in before the reaction is complete, otherwise a separation of unaltered benzil will occur. The crystals, after draining from the mother-liquor, should be washed with a small quantity of ether (which must be free from alcohol, since alcoholic potash has a specific action on the substance), then dissolved in ether, and the solution allowed to evaporate spontaneously. In this way the new compound is obtained in large colourless square prisms, frequently a quarter of an inch in thickness, with flattened ends and corners generally cut off. It is deposited from a hot alcoholic solution, on cooling, in small lustrous crystals. It is readily soluble in ether and in hot alcohol; but only moderately in cold alcohol. It melts at 78° . The powdered substance, after drying over sulphuric acid, is electric.

A further quantity of the substance can be obtained from the oily mother-liquors, but it was found more advantageous to treat these with an excess of strong potash, and in this way to obtain the condensation-compound dehydracetonebenzil, $C_{17}H_{14}O_2$ (*vide infra*), which, from its sparing solubility, can more readily be purified.

Analysis of the substance gave figures leading to the formula $C_{17}H_{16}O_3$:—

	Substance.		CO ₂ .	OH ₂ .
I.	0.1190		0.3306	0.0644
II.	0.1305		0.3634	0.0718
	Calculated for $C_{17}H_{16}O_3$.		Found.	
			I.	II.
C ₁₇	204	76.11	75.76	75.91
H ₁₆	16	5.97	6.01	6.11
O ₃	48	17.92	—	—
	268	100.00		

The substance is therefore an additive compound of benzil and acetone in equal molecular proportion (see Equation *a*, p. 21). It would receive the name *acetonebenzil*. (For the constitutional formula of this compound see p. 17.)

Dilute potash cannot be employed with advantage in the preparation of this compound. The reaction requires a longer time than with concentrated potash, and there is the additional drawback that a larger quantity of uncrystallisable oily substance is formed.

Action of Heat on Acetonebenzil.—A weighed quantity of substance

was introduced into a tubulated flask, which was connected with another similar flask, the latter to act as receiver. The flask with the substance was heated in a sulphuric acid bath, and the receiver was cooled with ice. A little below 200° , a few drops of liquid distilled over, and at 200° the liquefied substance in the flask boiled slowly, whilst a colourless liquid collected in the receiver. The heating was continued until nothing further distilled over. The dark-coloured residue, which solidified on cooling, was weighed; and the distillate was also weighed.

The residue was dissolved in hot alcohol. The solution, on cooling, deposited characteristic, yellow, needle-shaped crystals of benzil, melting at 94° .

The distillate had the odour of acetone, and on redistillation it boiled between 56° and 58° . Mixed with hydrogen sodium sulphite, it became hot, and, on cooling, the liquid deposited crystals of the acetone double compound.

The following are the quantitative results:—

Weight of substance	6.38 grams.
„ residue (benzil)	5.25 „
„ distillate (acetone)	1.10 „
Loss	0.03 „

Supposing the decomposition to have taken place according to the equation—



the weight of benzil obtained from the above weight of substance ought to have been 5 grams, and that of the acetone 1.38 grams. For an experiment of this kind, the above may be regarded as a sufficiently close approximation.

The decomposition is therefore analogous to that which acetone-phenanthraquinone undergoes under the influence of heat (Trans., 1882, 274).

Oxidation of Acetonebenzil.—The study of the oxidation of this compound was undertaken, less with a view of throwing light on its constitution than of comparing its behaviour towards oxidising agents with that of the condensation-product dehydracetonebenzil (*q.v.*).

By oxidation with a mixture of potassium dichromate and dilute sulphuric acid, the products obtained were benzoic and acetic acids. The formation of acetic acid is of importance in connection with the fact that the condensation-product yields no trace of acetic acid on oxidation.

We also attempted, by oxidising with chromic anhydride in acetic

acid solution, to obtain some intermediate product, but without success.

Action of Ammonia on Acetonebenzil.—20 grams of the compound were dissolved in ether, and the solution was saturated with dry ammonia. A separation of crystals commenced during the process, and, on standing, the quantity of crystalline substance increased. The liquid was poured off, the crystals washed with ether, and recrystallised from boiling alcohol, from which the compound was deposited in groups of small, colourless plates, melting at 176°. In melting, it turns red and evolves gas. The crystals also assume a faint pink colour by long exposure to the air. With hydrochloric acid and with oxalic acid, they yield a red gum.

Analysis gave results agreeing with the formula $C_{17}H_{17}NO_2$:—

	Substance.	CO ₂ .	OH ₂ .
I.	0.1316	0.3662	0.0784
II.	0.1468	0.4096	0.0880
III.	0.1228	0.3438	0.0730

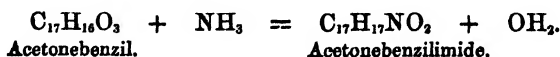
IV. 0.1104 gram burnt with cupric oxide in a vacuum gave 5.40 c.c. moist nitrogen at 14°, and under 756 mm. pressure.

V. 0.0886 gram gave 4.00 c.c. moist nitrogen at 14°, and under 759 mm. pressure.

	Calculated for $C_{17}H_{17}NO_2$.		Found.				
			I.	II.	III.	IV.	V.
C ₁₇	204	76.40	75.89	76.09	76.35	—	—
H ₁₇	17	6.37	6.61	6.66	6.60	—	—
N . . .	14	5.24	—	—	—	5.72	5.30
O ₂	32	11.99	—	—	—	—	—
	267	100.00					

Different preparations were employed in these analyses.

The following equation expresses the formation of this compound :—



This formation of *acetonebenzilimide*, as we propose to name the compound, corresponds with that of acetonephenanthraquinonimide (Trans., 1882, 274), from acetonephenanthraquinone and ammonia.

Action of Hydroxylamine on Acetonebenzil.—An attempt to prepare a hydroxylamine-derivative by heating the compound in alcoholic solution with hydroxylamine hydrochloride failed. The solution instantly became red on warming, and nothing but red resin was obtained. As

this was probably due to the action of the hydrochloric acid liberated in the reaction, the experiment was repeated, employing free hydroxylamine. For this purpose a quantity of acetonebenzil was dissolved in alcohol, and to this liquid a concentrated aqueous solution of two molecular proportions of hydroxylamine hydrochloride mixed with a slight excess of sodic carbonate, was added. After standing for two days, a considerable quantity of a white crystalline substance had separated. An excess of water was added in order to precipitate the organic substance and dissolve the inorganic salts. By recrystallisation from boiling alcohol, the new compound was obtained in small colourless crystals, melting at 146° . It is also moderately soluble in boiling benzene, but only sparingly soluble in ether. Hydrochloric acid converts it into a red resin.

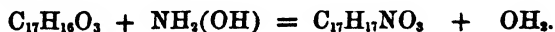
Analysis gave figures agreeing with the formula $C_{17}H_{17}NO_3$:—

	Substance.	CO_2 .	OH_2 .
I.	0.1371	0.3612	0.0756
II.	0.1114	0.2930	0.0616

III. 0.1070 gram burnt with cupric oxide in a vacuum gave 4.7 c.c. moist nitrogen at 17.7° , and under 763.5 mm. pressure.

	Calculated for $C_{17}H_{17}NO_3$.		Found.		
	I.	II.	I.	II.	III.
C_{17}	204	72.08	71.85	71.73	—
H_{17}	17	6.01	6.12	6.14	—
N	14	4.95	—	—	5.10
O_3	48	16.96	—	—	—
	283	100.00			

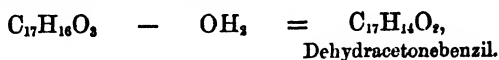
Only one molecule of hydroxylamine has therefore taken part in the condensation, and the formation of the compound is expressed by the equation—



All attempts to induce the compound thus obtained to react with a second molecule of hydroxylamine failed, although acetonebenzil must be assumed to contain two carbonyl-groups. This negative result is, however, in harmony with the investigations, since published, of Ceresole (*Ber.*, 17, 812), who shows that di-carbonyl compounds do not react with *two* molecules of hydroxylamine, unless the carbonyl-groups are directly united.

Action of Potash on a Solution of Acetonebenzil in Acetone.—A small quantity of the compound was dissolved in acetone, and an excess of strong potash (sp. gr. 1.27) added. After standing for a day, the

solution, which had become very dark, was poured into water. The substance which separated was dried and then recrystallised from boiling benzene. It was thus obtained in yellow crystals, melting at 147° , and proved to be dehydracetonebenzil, a condensation-product of benzil with acetone described later on. The reaction had therefore taken place according to the equation—



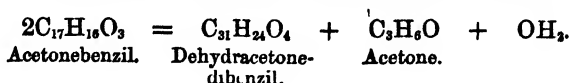
and no diacetone compound had been formed as in the case of the corresponding phenanthraquinone reaction.

Action of Dilute Alcoholic Potash on Acetonebenzil.—From 4 to 5 grams of the compound were dissolved in sufficient alcohol to keep the substance in solution in the cold, 5 drops of concentrated alcoholic potash were added, and the whole was allowed to stand in a corked flask. The solution assumed a light-red colour, and colourless lustrous crystals were gradually deposited on the sides of the flask. These were washed with alcohol and then recrystallised from benzene until the constant melting point $194\text{--}195^{\circ}$ was obtained.

Analysis led to the formula $\text{C}_{31}\text{H}_{24}\text{O}_4$:—

Substance.	CO_2 .		OH_2 .
0.1462	0.4322		0.0692
	Calculated for $\text{C}_{31}\text{H}_{24}\text{O}_4$.		Found.
C_{31}	372	80.87	80.62
H_{24}	24	5.21	5.19
O_4	64	13.92	—
	460	100.00	

The compound is identical with one described later on (dehydracetone-dibenzil) obtained by the action of potash on a mixture of acetone with excess of benzil (see also Equation c, p. 21). The reaction in which it is formed in the present case differs from the reaction of alcoholic potash with acetonephenanthraquinone (p. 20), inasmuch as with the quinone compound there was elimination of acetone only, whereas in the present case both acetone and water are eliminated:—



The action of various other reagents—phosphoric chloride, acetic anhydride, nascent hydrogen—was tried, but without yielding any definite result.

b. *Action of an Excess of strong Potash on a Mixture of Benzil with an Excess of Acetone.*

100 grams of pure acetone, 150 grams of finely powdered benzil, and 1 c.c. of potash solution (sp. gr. 1.27) were introduced into a flask, and shaken until all the benzil had dissolved; after which 20—30 c.c. of the potash solution were added, and the whole, after thoroughly shaking, was allowed to stand for a day. At the end of this time, the layer of acetone and benzil floating on the surface of the excess of potash had solidified. The potash was poured off, and the contents of the flask were shaken with hot water, which melted the crude product and removed the remains of the potash. The product, which solidified on cooling, was ground in a mortar, extracted in a flask with a small quantity of ether, and then washed on a filter with ether until the filtrate passed through only slightly coloured. In this way, the dark-coloured impurities were for the most part removed. The yellowish-grey powder thus obtained was crystallised from hot alcohol or benzene until the constant melting point 147° was obtained. The alcoholic solution deposits the compound in large, canary-yellow* prisms; from benzene it separates in tufts of needles of the same colour.

Animal charcoal had no effect in removing this colour, nor could the above melting point be altered by recrystallisation. The appearance of the compound was perfectly homogeneous, and we had no reason to suspect the presence of an impurity, especially as analysis gave figures agreeing well with those required for a condensation-product of 1 mol. benzil with 1 mol. of acetone, formed with elimination of 1 mol. of water. In an experiment, however, to be described later, in which the substance was oxidised with chromic anhydride in acetic acid solution, there was obtained, along with a new acid, a colourless neutral substance, which was deposited from benzene in forms indistinguishable from those of the above yellow compound, but melting at 149° . On analysis this colourless compound gave figures agreeing with the formula deduced for the yellow compound. The oxidation had therefore removed from the supposed yellow compound a coloured impurity, and had at the same time slightly raised the melting point. In order to dispel any doubt as to the identity of the white and yellow compounds, a mixture of the two was dissolved in benzene. Crystals of a paler yellow colour were deposited, not a mixture of white and yellow crystals.

The following are the analytical results, which lead to the formula $C_{17}H_{14}O_2$:—

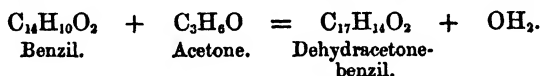
* See, however, following paragraph.

	Substance.	CO ₂ .	OH ₂ .
I	0.1176	0.3502	0.0614
II	0.1234	0.3679	0.0638
III	0.1330	0.3978	0.0686
IV	0.1348	0.4034	0.0700

	Calculated for C ₁₇ H ₁₄ O ₂ .		Found.			
			I.	II.	III.	IV.
C ₁₇	204	81.60	81.21	81.31	81.57	81.61
H ₁₄	14	5.60	5.80	5.74	5.74	5.77
O ₂	32	12.80	—	—	—	—
	<hr/>	<hr/>				
	250	100.00				

Analyses I and II were made with the yellow substance; III and IV with the colourless substance.

The formation of the compound is expressed by the equation—

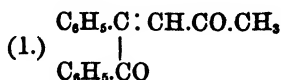


In all probability acetonebenzil is formed as an intermediate product. The conversion of acetonebenzil into this compound has been already described (p. 25). As the new compound is derived from acetonebenzil by the removal of a molecule of water, we propose to name it *dehydracetonebenzil*. It is worthy of note that this conversion cannot be effected by means of acetic anhydride.

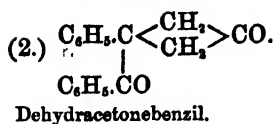
As regards the constitution of dehydracetonebenzil, *apparently* the most natural supposition would be to regard it as an analogue of Claisen and Ponder's benzalacetone,



(*Annalen*, 223, 138), obtained by the condensation of benzaldehyde with acetone under the influence of dilute caustic soda. According to this view, it would be a benzoyl-derivative of benzalacetone and would possess the formula—



The behaviour of this compound with bromine and with oxidising agents is, however, quite incompatible with this view. Its behaviour with oxidising agents can best be accounted for by the supposition that it is a closed-chain compound of the formula—



(See also p. 13.)

*Action of Bromine on Dehydracetonebenzil.**—10 grams of the compound were dissolved in sufficient chloroform to keep the whole in solution in the cold, and a solution of bromine in chloroform was gradually added. The colour of the bromine did not disappear. After standing for some time, fumes of hydrobromic acid were given off, and a crystalline substance was deposited. Both the chloroform and the bromine had been carefully dried before using.

The crystalline substance was washed with chloroform and recrystallised from hot glacial acetic acid, from which it was deposited on cooling in slender colourless needles, melting at 172° with blackening and decomposition. It is only sparingly soluble in alcohol.

Two bromine determinations (method of Carius) gave figures pointing to a monobromo-substitution compound:—

	Substance.	AgBr.
I	0.2872	0.1627
II	0.2538	0.1458

	Calculated for $\text{C}_{17}\text{H}_{13}\text{BrO}_2$.	Found.	
		I.	II.
Br in 100 parts	24.21	24.10	24.44

In order to make perfectly sure that this monobrominated compound had not been obtained from a dibromide by decomposition during recrystallisation, a fresh quantity of the substance was prepared, washed thoroughly with cold chloroform, dried at ordinary temperatures, and then analysed. This preparation gave 26.2 per cent. of bromine, showing it to be merely an impure monobromo-compound.

A compound of formula (1) ought, judging from the analogy of benzalacetone and the other compounds prepared by Claisen, to yield a dibromide. That dehydracetonebenzil has not this formula is rendered still more probable by the fact that dehydracetophenonebenzil (*q.v.*), in which the substitution of phenyl for methyl appears to have prevented the formation of a closed chain, and which has a constitution corresponding with formula (1), readily forms an additive compound with bromine.

* For all reactions here described, the yellow compound was employed.

Oxidation of Dehydracetonebenzil.—20 grams of the yellow compound were dissolved in glacial acetic acid, and an equal weight of chromic acid—also dissolved in acetic acid—was gradually added. The mixture, which became slightly warm, was finally boiled with a reflux condenser in order to finish the reaction. It was then poured into water, which occasioned a separation of organic substance. The whole was extracted with ether, and the ethereal solution was shaken with a solution of sodium carbonate in order to remove acids. On evaporating the ether, some unattacked dehydracetonebenzil was obtained, but in a *colourless* condition.

The sodium carbonate solution was acidified with hydrochloric acid and extracted with ether. On distilling off the ether, an acetic acid solution of a new organic acid remained behind, and, by allowing the acetic acid to evaporate in a desiccator over lime, the new acid was obtained in almost colourless crystals, whilst any benzoic acid that had been formed remained in the mother-liquor. The acid was recrystallised from boiling benzene until it showed a constant melting point. Thus purified, it forms tufts of colourless needles, melting at 152° . It is readily soluble in boiling benzene, but separates almost entirely on cooling. Boiling water dissolves it sparingly.

Analysis gave the following results:—

	Substance.	CO ₂ .	OH ₂ .
I.....	0.1331	0.3682	0.0672
II.....	0.1276	0.3530	0.0642

These numbers lead to the formula C₁₆H₁₄O₃:—

	Calculated for C ₁₆ H ₁₄ O ₃ .		Found.	
			I.	II.
C ₁₆	192	75.59	75.44	75.44
H ₁₄	14	5.51	5.61	5.59
O ₃	48	18.90	—	—
	254	100.00		

A *silver salt* was prepared by precipitating a solution of the ammonium salt with silver nitrate. It forms a white powder. The dry salt is electric. It gave the following figures on combustion:—

Substance.	CO ₂ .	OH ₂ .	Ag.
0.1418	0.2752	0.0466	0.0424

	Calculated for $C_{16}H_{14}O_3$ Ag.		Found.
C_{16}	192	53.18	52.92
H_{14}	13	3.60	3.64
Ag.....	108	29.92	29.90
O_3	48	13.30	—
	361	100.00	

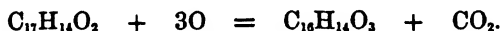
The *barium salt* was obtained by boiling the acid with *barium carbonate*, and allowing the solution to evaporate over sulphuric acid. Like all the soluble salts of this acid which we examined, its difference of solubility in hot and cold solutions is very slight. It was obtained in rosettes of flat prisms of the formula $(C_{16}H_{14}O_3)_2Ba, 2OH_2$. It parts with its water of crystallisation at 100° .

0.3064 gram of air-dried salt lost at 100° 0.0160 gram, and the resulting 0.2904 gram anhydrous salt gave 0.1042 gram barium sulphate.

	Calculated for $(C_{16}H_{14}O_3)_2Ba, 2OH_2$.	Found.
OH_2 in 100 parts	5.30	5.22

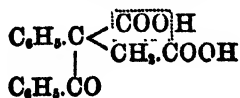
	Calculated for $(C_{16}H_{14}O_3)_2Ba$.	Found.
Ba in 100 parts	21.30	21.09

The acid is formed from dehydracetonebenzil according to the equation—

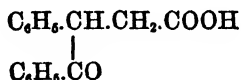


Supposing dehydracetonebenzil to possess the constitution represented by formula (1), the oxidation of such a compound to an acid of the formula $C_{16}H_{14}O_3$ would be very difficult to account for. It would be necessary to assume that the methyl-group at the end of the chain is oxidised away, the carbonyl-group converted into carboxyl, and that then the two unsaturated carbon-atoms, under conditions which generally lead to the separation of such atoms, take up, in presence of a powerful oxidising agent, hydrogen and become saturated.

On the other hand, by adopting formula (2) for dehydracetonebenzil, the formation of the acid can be explained. In the first place by a separation of the carbonyl from one of the methylene-groups in the closed chain, and by conversion of these separated groups into carboxyl-groups, an acid of the formula



would be obtained. This acid is a bibasic ketonic acid. It is well known that ketonic acids vary greatly in stability according to the class to which they belong. Those ketonic acids are stable in which carboxyl and carbonyl are directly united, as in pyruvic acid, or in which carboxyl and carbonyl are attached to different carbon-atoms, as in lævulic (β -acetylpropionic) acid; those are unstable, in which carboxyl and carbonyl are attached to the same carbon-atom, as in the case of acetoacetic acid: such acids readily part with carbonic anhydride, yielding a ketone. An acid of the above formula would unite in itself the properties of two of the above classes; it would be unstable as regards the carboxyl-group attached to the same carbon-atom as the benzoyl-group; and it would be stable as regards the other carboxyl-group. Under the conditions of the oxidation experiment, this acid would part with carbonic anhydride from the first of these carboxyl-groups (as indicated in the formula), yielding the monobasic acid:—



which would thus be β -benzoylhydrocinnamic acid.

Although we regard the above as the most probable of the various constitutional formulæ that might be suggested for the acid, we must call attention to the fact that the only reactions which we have tried in confirmation of this constitution have yielded negative results. Thus, by the action of nascent hydrogen we hoped to obtain a lactone; but after subjecting the acid for some days to the action of sodium-amalgam, nearly the whole of the original substance was recovered unchanged, and only a trace of an indifferent oil was formed, which, however, did not appear to be a lactone, as it did not dissolve in caustic alkalis on heating.* We further hoped, by the action of hydroxylamine, to prove the ketonic character of the acid; but no action took place with hydroxylamine hydrochloride in aqueous alcoholic solution at 100°.

The various other constitutions that might be suggested for this acid—thus that it is an acid of the glycidic type, or that it is an unsaturated acid containing an alcoholic hydroxyl-group—are still less in keeping with its reactions and mode of formation.

The chief obstacle to a thorough study of this acid is the difficulty of obtaining it in any considerable quantity, the yield being very small.

As a dehydracetonebenzil of formula (1) ought to yield acetic acid on oxidation, it seemed of importance to show that this acid was not

* Of course this insolubility in caustic alkalis does not absolutely prove that the oil was not a lactone.

formed, especially as acetonebenzil readily yields acetic acid. A quantity of dehydracetonebenzil was therefore boiled with a mixture of dilute sulphuric acid and potassium dichromate, until all action had ceased. The liquid was then distilled until about a third had passed over; the distillate was filtered from benzoic acid, neutralised with sodium carbonate, and evaporated to dryness. Not the slightest trace of acetic acid could be obtained from this residue.

Another portion of dehydracetonebenzil was oxidised with a 5 per cent. permanganate solution in the cold. The filtrate from the manganese dioxide, when acidified and extracted with ether, yielded as chief product benzoic acid, along with a small quantity of benzoylformic acid, identified by means of the characteristic thiophene reaction. We satisfied ourselves that β -benzoylhydrocinnamic acid does not give this reaction.

The action of the following reagents upon dehydracetonebenzil was also tried, but without definite result:—acetic anhydride, alcoholic ammonia, potash (fusion), hydriodic acid and amorphous phosphorus, zinc-dust at higher temperatures, zinc-dust with acetic acid.

c. Action of a Small Quantity of Potash on a Mixture of Acetone with Excess of Benzil.

50 grams of finely powdered benzil were introduced into a flask with 20 grams of pure acetone and $\frac{1}{2}$ c.c. of potash solution (sp. gr. 1.27). The flask was shaken until all the benzil had dissolved, this process requiring about an hour. After standing for a day, the contents of the flask, which were almost solid, were shaken with ether. A small quantity of acetonebenzil went into solution and a sparingly soluble white crystalline powder remained, which, after washing with ether, was recrystallised from benzene until the constant melting point $194-195^{\circ}$ was obtained.

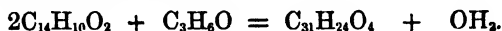
Besides acetonebenzil, the ethereal washings contained an uncrystallisable gum, which, however, by shaking with more potash, could be converted into the sparingly soluble crystalline compound.

Analysis gave results agreeing with the formula $C_{21}H_{24}O_4$:—

	Substance.	CO ₂ .	OH ₂ .
I.	0.1194	0.3520	0.0570
II.	0.1420	0.4182	0.0666
III.	0.1656	0.4874	0.0790

	Calculated for $C_{31}H_{24}O_4$		Found.		
			I.	II.	III.
C_{31}	372	80.87	80.40	80.32	80.27
H_{24}	24	5.21	5.30	5.21	5.30
O_4	64	13.92	—	—	—
	460	100.00			

The compound is identical with that obtained by the action of dilute alcoholic potash on acetonebenzil (p. 26). Its formation in the present case occurs by the abstraction of 1 mol. of water from 2 mols. of benzil and 1 mol. of acetone. It would therefore receive the name *dehydracetonedibenzil* :—



Dehydracetonedibenzil is almost insoluble in cold benzene and alcohol; even boiling alcohol dissolves it but sparingly. The best solvent is boiling benzene, from which it is deposited, after some time, in well-formed colourless crystals. From the alcoholic solution, it separates with 1 mol. of alcohol of crystallisation, which is retained at 100°, but given off at 120°. When the crystals containing alcohol of crystallisation are heated in a capillary tube they melt at 158—160°.

Alcohol of crystallisation was determined with the following result :—

0.2410 gram air-dried substance, containing alcohol of crystallisation, lost at 120° 0.0222 gram.

	Calculated for $C_{31}H_{24}O_4, C_2H_6O$	Found.
C_2H_6O in 100 parts	9.09	9.21

3. BENZIL AND ACETOPHENONE.

a. Action of Potash in the Cold on a Mixture of Benzil and Acetophenone.

Equal molecular proportions of acetophenone and finely powdered benzil were shaken in a flask with an excess of strong potash (sp. gr. 1.27) and allowed to stand. At first the potash solution remained in suspension, but after a few days it separated, whilst the organic substance formed a solid cake on the surface. This cake was ground with water, thoroughly washed, and, after drying, shaken with ether. The greater part dissolved, leaving a yellow powder, which proved to be dehydracetophenonebenzil, a compound to be described later. On spontaneous evaporation, the ethereal solution deposited large colourless oblique prisms, and the mother-

liquor from these crystals yielded a further quantity of the same substance, contaminated however with unchanged benzil. By crystallisation from alcohol, the colourless substance was obtained pure in flat oblique prisms, melting at 102° . It is readily soluble in ether and in boiling alcohol, sparingly soluble in alcohol in the cold. When heated above its melting point, it gives off acetophenone, which may be recognised by its odour.

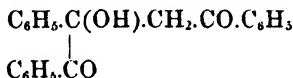
Analysis gave numbers agreeing with the formula $C_{22}H_{18}O_3$:—

	Substance.	CO ₂ .	OH ₂ .
I.....	0.1426	0.4170	0.0724
II.....	0.1498	0.4378	0.0756
	Calculated for $C_{22}H_{18}O_3$.		Found.
			I. II.
C ₂₂	264	80.00	79.75 79.70
H ₁₈	18	5.45	5.64 5.60
O ₃	48	14.55	— —
	<hr/>	<hr/>	
	330	100.00	

The formation of this compound is expressed by the equation —



and it would receive the name *acetophenonebenzil*. Its constitutional formula would be—



b. Action of Potash, aided by Heat, on a Mixture of Benzil and Acetophenone.

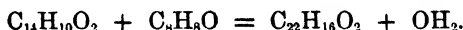
The ingredients were mixed as in the preceding experiment; but heat was applied until the whole of the benzil had fused, after which the flask was allowed to stand for some hours at a temperature sufficiently high to prevent solidification. On allowing the flask to cool, the layer of organic substance floating on the surface of the potash solidified. The solid cake was treated as in the former experiment. This time, the ethereal extract contained only a small quantity of a reddish oil and a trace of unaltered benzil. No acetophenonebenzil was formed on this occasion. The portion undissolved by the ether was recrystallised from hot alcohol, until it exhibited the constant melting point 129° . It crystallises in tufts of flat pointed yellowish needles, which are very sparingly soluble in ether and in cold alcohol, but dissolve readily in boiling alcohol.

The analytical figures agreed with the formula $C_{22}H_{16}O_2$:—

	Substance.	CO_2 .	OH_2 .
I.	0.1582	0.4900	0.0748
II.	0.1296	0.4010	0.0628

	Calculated for $C_{22}H_{16}O_2$		Found.	
			I.	II.
C_{22}	264	84.61	84.47	84.38
H_{16}	16	5.13	5.25	5.38
O_2	32	10.26	—	—
	312	100.00		

This compound is formed by the condensation of a molecule of benzil with a molecule of acetophenone :—



It may therefore receive the name *dehydracetophenonebenzil*.

Action of Bromine on Dehydracetophenonebenzil.—The compound was dissolved in cold chloroform, avoiding an excess of the solvent, and one molecular proportion of bromine was added. On standing, the colour due to the bromine gradually became much fainter, without however entirely disappearing, and a bromine-derivative was deposited in large crystals. There was no evolution of hydrobromic acid. The crystals were of a reddish colour, and, when exposed to the air, gave off a faint odour of bromine, even after standing for some days, at the same time becoming opaque. As it was found impossible to re-crystallise this substance without decomposition, the freshly prepared crystals were washed with chloroform, exposed for a short time to the air, powdered, the powder dried for two hours over sulphuric acid, and in this condition analysed. A bromine estimation (Carius) gave figures which were somewhat too high for a *tetrabromide*—an entirely unexpected result.

0.1864 gram of substance gave 0.2278 gram of silver bromide.

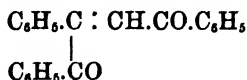
	Calculated for $C_{22}H_{16}O_2Br_4$.	Found.
Br in 100 parts.	50.63	52.00

Heated in a capillary tube the substance becomes dark at about 70° , turns pale again at about 80° , and melts between 110° and 115° .

The bromine was in a state of very unstable combination. A portion of the substance which had been allowed to remain for some weeks in a desiccator over lime, had parted with nearly the whole

of its bromine, and was found, after recrystallisation from alcohol, to have been reconverted into dehydracetophenonebenzil.

We are unable satisfactorily to explain the formation of a tetrabromide. A dehydracetophenonebenzil of the formula—



ought to yield a dibromide, and it is conceivable that this dibromide might form a molecular compound with a second molecule of bromine, similar to the molecular compounds of acetic acid with bromine and hydrobromic acid. In any case, the action is anomalous and deserves further study. For the present, however, we regard this reaction as sufficient evidence of the unsaturated character of dehydracetophenonebenzil, and the foregoing is the only probable constitutional formula which would represent it as an unsaturated compound.

The fusing points of dehydracetonebenzil and dehydracetophenonebenzil also render it probable that these compounds do not belong to one and the same category. Whereas acetophenonebenzil, a compound which may be regarded as derived from acetonebenzil by the substitution of phenyl for methyl, fuses higher than acetonebenzil, dehydracetophenonebenzil fuses 20° lower than dehydracetonebenzil. The high melting point of the latter compound is probably due to the fact that it is, as assumed in this paper, a closed-chain compound.

*Normal School of Science,
South Kensington.*

III.—On some New Paraffins.

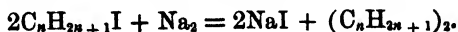
By KHAN BAHADUR BOMANJI SORABJI, Ph.D., C.E., &c.

At present, comparatively little is known of the higher members of the paraffin series; the difficulty of separating them from one another rendering it impossible to isolate them from their natural sources, such as petroleum, ozokerit, &c. The solid paraffin obtained from such sources can be partly separated into its constituents by means of fractional crystallisation, but the fractions thus prepared are still far from being homogeneous and pure compounds.

In order to study these higher paraffins, therefore, it is necessary to prepare them synthetically. Several syntheses of this kind have

lately been made by Krafft (Abstr., 1882, 1271 and 1272), but many gaps in the series of paraffins still remain, and the present communication gives the results of an endeavour to prepare some of the missing members of the series.

The method which appeared most likely to yield satisfactory results was that of Würtz, which consists in treating the iodide of an alcohol radicle with sodium, according to the equation—



But in these reactions more or less of the paraffin containing the same number of carbon-atoms as the alcohol radical is almost always produced, according to the equation—



As my especial aim was the preparation of dicetyl, $C_{32}H_{66}$, and the paraffin cetane, $C_{16}H_{34}$, which would probably be produced as a by-product, had not been prepared from cetyl iodide, it appeared of interest first to make and examine this body so as to minimise, as far as possible, the after difficulty of the purification of the dicetyl.

I. Cetane from Cetyl Iodide.

This paraffin was obtained from the iodide by the reduction of the latter by concentrated hydriodic acid in the presence of phosphorus, and also by the digestion of the iodide with zinc and hydrochloric acid.

Cetyl iodide was mixed with four times its weight of pure alcohol, and introduced into a flask containing a considerable quantity of granulated zinc, the flask being connected with a reflux condenser. Fuming hydrochloric acid was then slowly added, causing at once a precipitation of a heavy oil (cetyl iodide). After four or five days' digestion, the oil rose to the top of the liquid, but as it still contained much iodine it was resubjected to the same treatment for a week. Water was then added, and the oil which separated was washed repeatedly with concentrated sulphuric acid containing nitric acid, with water, with caustic soda, and with water until it no longer contained a trace of iodine. It was then dried over solid potash and distilled. Cetane, thus obtained, boils constantly at 278° , and when cooled, solidifies to a crystalline mass which melts at $18-20^\circ$. A combustion yielded the results—

	Calculated.			Found.
C_{16}	192	84.96	per cent.	84.76
H_{34}	34	15.04	,,	15.29

Two vapour-densities made with V. and C. Meyer's apparatus yielded 7.9 and 7.85 respectively, theory requiring 7.84. Zincke's dioctyl (*Annalen*, 152, 16) from primary octyl iodide melted at 21°, and the same body obtained from mercury octyl by Eichler (*Ber.*, 12, 1882) had a melting point of 14°. Cetane resembled Zincke's dioctyl in all other respects, and its low melting point, as well as that of Eichler's compound, is probably due to the presence of a trace of impurity.

Cetane is miscible in all proportions with alcohol and ether: and as cetene is also very soluble in these reagents, the purification of dicetyl from these bye-products did not seem to offer any difficulty.

II. Dicetyl from Cetyl Iodide.

Cetyl iodide dissolved in six times its weight of ether was introduced into a flask connected with a reflux condenser. Finely cut sodium was then added, and the whole allowed to stand for some time at the ordinary temperature. Action set in rapidly, the metal became coated with sodium iodide, and iridescent flakes were deposited in the liquid. The reaction was completed by heating the mixture for 10 hours on the water-bath. On cooling, no trace of cetyl iodide could be detected, but the whole liquid became filled with beautiful glistening scales. In order to remove excess of sodium, alcohol was added, and after the evolution of hydrogen had ceased, the precipitated sodium iodide was dissolved by the addition of water. The whole was then thrown on a filter and the residual crystalline mass dried, and extracted with boiling absolute alcohol, in which it is almost insoluble. Dicetyl is also nearly insoluble in ether, but dissolves readily in boiling glacial acetic acid, crystallising out again almost entirely on cooling. When recrystallised twice from acetic acid, it melts at 70° and distils undecomposed, but at a temperature lying far above the range of the mercury thermometer. On cooling, the distillate solidifies to beautiful pearly scales. Dicetyl is neither dissolved nor blackened when treated with concentrated sulphuric acid at 150°.

Combustions yielded the following results:—

- I. 0.1655 gram subs. gave 0.5138 gram CO₂ and 0.2197 gram H₂O.
 II. 0.1470 " " 0.4592 " 0.1956 "

These yield the numbers—

	Calculated.	Found.
C ₂₂ =	384 = 85.33	85.18 85.19
H ₄₄ =	66 = 14.67	14.84 14.78

Vapour-densities conducted by means of V. and C. Meyer's apparatus gave the numbers:—

- I. 0.2354 gram substance gave 12.56 c.c. air at 18° and 743.9 mm. pressure.
- II. 0.2332 gram substance gave 13.10 c.c. air at 23° and 746.1 mm. pressure.
- III. 0.0929 gram substance gave 5.20 c.c. air at 23° and 746.1 mm. pressure.

The results when calculated out give—

	Calculated.	Found.		
		I.	II.	III.
$C_{32}H_{66}$	15.5	16.1	15.64	15.70

The mother-liquors from the crude dicetyl yielded, on evaporation, a very slight crystalline residue, which proved to be almost entirely dicetyl. It is thus clear that hardly any bye-products are formed in this reaction.

III. *Ethyl-cetyl from Ethyl and Cetyl Iodides.*

This compound was obtained by allowing sodium, cut in thin flakes, to act on a mixture of ethyl and cetyl iodides dissolved in ether. The reaction was slower than when cetyl iodide alone was used. A good deal of dicetyl was formed, but the etheric liquid contained a second body, which, on evaporation of the ether, remained as a colourless oil. After purification with sulphuric acid, &c., as before, this oil was dried with solid potash and distilled, when it passed over at 312–313°, and the distillate solidified when cooled with ice. This substance was undoubtedly ethyl-cetyl, but the quantity obtained was too small for a combustion or vapour-density determination. It is also doubtful whether it was quite pure, so that the above boiling point must only be looked upon as approximate.

IV. *Diheptyl from Heptyl Iodide.*

Although heptyl alcohol can be prepared without great difficulty from cœnanthaldehyde, and the iodide is very easily obtainable from the alcohol, on attempt appears yet to have been made to synthesise the normal paraffin of the formula $C_{14}H_{30}$ from this iodide. It was thought that the synthesis of normal diheptyl might prove of some interest.

The heptyl alcohol employed was prepared from cœnanthaldehyde in part by Cross's method (*Chem. Soc. J.*, 1877, 32, 124), as modified

by Jourdan (*Annalen*, 200, 102), in part by Krafft's method for the reduction of aldehydes of high molecular weight (*Abstr.*, 1883, 1075). According to the first-named process, a solution of the aldehyde in glacial acetic acid is reduced by means of sodium-amalgam; according to the second, a similar solution is employed, but zinc-dust takes the place of sodium-amalgam. A better yield of alcohol and a smaller admixture of bye-products was obtained by the first than by the second process. The heptyl alcohol boiled at 175.5° , and gave satisfactory numbers on analysis. It was converted into the iodide by saturating it with gaseous hydriodic acid (Möslinger, *Annalen*, 185, 55). The pure iodide boiled at 201° .

The conversion of the iodide into the paraffin was effected in a manner precisely similar to that employed in the case of dicetyl. The reaction was completed at the ordinary temperature in about three days.

Diheptyl, prepared in this way, is a colourless mobile oil having a slight odour. It boils without decomposition at 245° under 750 mm. pressure. When cooled by means of ice, it solidified to a lamellar crystalline mass, which began to melt again at 6° , and was completely liquid at 10.5° .

Analysis yielded the following results:—

0.1880 gram substance gave 0.5831 gram CO_2 and 0.2616 gram H_2O .

	Calculated.		Found.
C_{14}	168	84.80 per cent.	84.58
H_{30}	30	15.20 „	15.47

Vapour-density determinations gave the numbers—

- I. 0.0602 gram substance gave 7.40 cm. air at 21° and 747.2 mm. pressure.
- II. 0.0429 gram substance gave 5.35 cm. air at 28° and 746.1 mm. pressure.

These numbers when calculated out give 7.06 and 7.04 respectively, whilst theory requires for the formula $\text{C}_{14}\text{H}_{30}$, 6.82.

In conclusion, I have to express my thanks to Professor Johannes Wislicenus, at whose suggestion and in whose laboratory this work was carried out, both for the interest he has taken in my work, and for the valuable advice he has given me during its progress.

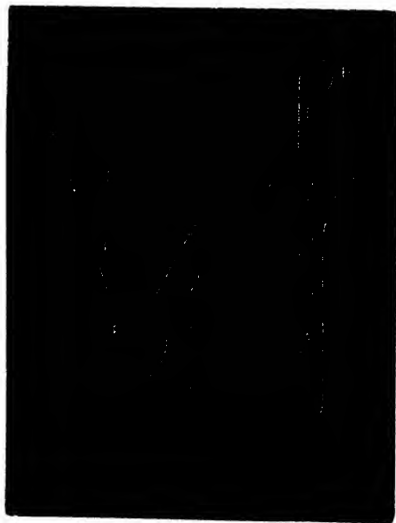
IV.—*On a New Method of Determining the Vapour-pressures of Solids and Liquids, and on the Vapour-pressure of Acetic Acid.*

By WILLIAM RAMSAY, Ph.D., and SYDNEY YOUNG, D.Sc.

IN determining the vapour-pressure of acetic acid, Regnault (*Mémoires de l'Académie*, 1862, **26**, 51—60) found at 0° numbers varying between 3.23 mm. and 4.9 mm., whilst Landolt (*Annalen*, Suppl. VI, 157) gave 7.6 mm.; at 10°, Regnault gave numbers differing as much as 6.3 and 8.2 mm., and at that temperature Landolt found 12.1 mm.; at 15° the difference is still more striking, for the pressure given by Bineau (*Annales de Chimie* [3], **18**, 226) is 7 mm., by Regnault 8.7 to 10.4 mm., and by Landolt 15.1; while at 14°, Wüllner (*Pogg. Ann.*, **103**, 529) observed a pressure of 15.7 mm. No one has attempted to account for these discrepancies, except Regnault, who supposed his variations to be due to the presence of acetone when the vapour-pressure was high, and of water when low.

In the course of an investigation "On the Temperature of Volatilisation of Solids (*Trans. Roy. Soc.*, Part I, 1884, p. 37), a method of ascertaining the vapour-pressure of liquids, differing essentially from the one usually employed, was devised, of which the following is a description:—

A is a vertical tube, closed at the top by an accurately fitting india-rubber cork perforated with two holes, through one of which a



thermometer passes, the bulb of which is completely covered with cotton-wool, adhering closely when moist. Through the other hole is inserted a short narrow glass tube, drawn out to a point at its lower end, and slightly curved so that the point touches the thermometer.

To the other end of this tube is connected by india-rubber tubing a small reservoir, B; the passage of liquid from B is controlled by means of a screw-clip. It is thus possible to allow liquid to enter the apparatus, trickling down the thermometer and soaking the cotton-wool. At C a tube, 15 mm. in diameter, is sealed on to the vertical tube. The tube C communicates with the condenser E; near the point of junction an exit-tube, F, leads to a Sprengel pump. On one side of the exit-tube, a narrow tube, D, is sealed. This narrow tube is for the purpose of admitting air into the apparatus, and is closed by a short piece of india-rubber tubing and a screw-clip.

The tube A may be heated either by hot water or paraffin, or it may be jacketed with a wider tube, as shown in the figure, and exposed to the vapour of any desired liquid. The condenser, E, may be cooled with a freezing mixture, especially if the liquid is volatile.

The actual experiment is performed by exhausting the apparatus as perfectly as possible with a Sprengel's pump, to which a gauge is attached; by unscrewing the screw-clip, liquid enters the apparatus, trickles down the thermometer, and thoroughly moistens the cotton-wool. When a sufficient quantity has entered, the screw-clip is closed. The tube is then heated, and the temperature and pressure noted as soon as they have become constant. A little air is admitted by means of the clip at D, and the pressure and temperature again read off. When the supply of liquid on the cotton-wool has become exhausted, more of the liquid is admitted. This process is repeated until a sufficient number of observations have been taken. The results may be checked by beginning at a high pressure, and gradually exhausting the apparatus with the pump, reading whenever convenient.

We think that this process has advantages over the usual one, inasmuch as the temperature of the whole apparatus has not to be kept constant, and the pressure can be regulated as desired, and a great number of observations taken; moreover, the extreme difficulty of introducing a liquid free from air into a barometer tube is avoided. We are induced to think that the presence of air and moisture is the cause of most of the discrepancies in the results obtained by different observers.

This method is equally applicable to the determination of the vapour-pressure of solids, by substituting a cork perforated with one hole instead of two, and coating the thermometer with the solid, by dipping it repeatedly into the melted substance. The only precaution required is to avoid dipping the bulb E so deeply into the freezing-mixture as

to block the exit-tube by condensation of the solid. Results proving the accuracy of this process have already been communicated in the paper previously referred to.

The results obtained by this process of determining vapour-pressures agreed closely, in the case of water, with Regnault's results. We are therefore confident that the following numbers for acetic acid closely approximate to the truth. Moreover, as will be pointed out in a subsequent paper, the curve for acetic acid given by this process is abso-

Vapour-pressure of Acetic Acid.

Solid.		Liquid.		Liquid.	
Temp.	Pres.	Temp.	Pres.	Temp.	Pres.
- 5·68°	1·3 mm.	2·72°	4·00 mm.	36·9°	28·9 mm.
- 0·60	1·95	4·20	4·25	40·1	34·3
+ 1·85	2·35	4·70	4·75	43·8	41·7
2·86	2·80	6·30	5·00	48·2	51·3
5·32	3·30	7·06	5·25	48·5	51·7
6·30	3·70	7·13	5·40	49·2	53·7
6·41	3·75	8·54	5·95	49·65	55·6
6·68	3·85	8·58	5·95	50·5	58·1
7·09	4·00	9·70	6·20	53·5	66·7
7·20	4·05	10·60	6·50	57·4	78·7
8·40	4·25	10·70	6·75	59·6	87·6
8·50	4·35	12·30	7·30	61·8	96·3
8·72	4·60	13·70	8·10	68·5	127·5
9·16	4·70	14·20	8·30	69·1	131·9
10·40	5·30	14·39	8·45	71·6	146·3
11·39	5·75	14·72	8·50	78·2	156·2
11·70	6·15	14·90	8·55	76·4	177·3
12·10	6·05	15·50	9·10	78·8	194·4
12·20	6·05	15·60	9·15	79·8	199·5
12·60	6·65	15·70	9·35	81·65	215·2
13·30	6·75	16·75	10·45	83·4	228·0
13·96	7·30	17·00	9·75	83·9	236·3
14·30	7·20	18·60	11·10	84·6	242·1
14·58	7·95	19·20	11·05	87·5	267·8
14·85	8·00	20·10	12·00	91·4	307·9
15·15	8·40	20·90	12·45	94·5	341·3
15·40	8·75	21·40	12·65	97·4	376·4
15·60	8·55	21·68	12·85	98·6	396·8
15·80	8·85	22·05	13·05	100·6	425·2
16·09	8·95	22·40	12·90	103·3	460·3
16·20	9·10	23·00	13·65	105·45	501·8
16·32	9·15	23·40	13·80	107·45	540·0
16·41	9·45	25·60	15·95	110·4	587·1
		27·20	16·80	112·4	623·8
		27·30	17·45	113·4	642·6
		31·80	21·80	114·1	657·5
		32·70	22·90	117·15	717·9
		36·10	28·30		

tutely coincident with that obtained by the usual process, when air and moisture were rigorously excluded, and when an absolutely pure specimen was employed.

These results, which are here arranged in order, were obtained in eight different series, for each one of which the acetic acid was fractionated from a large stock.

From the numbers, the following results were obtained by graphic interpolation; it may be interesting to compare them with results obtained by Regnault, by Landolt, and by Wüllner.

Temp.	Ramsay and Young.		Regnault.	Landolt.	Wüllner.
	P. (solid).	P. (liquid).	Pres.	Pres.	Pres.
0°....	2.02	3.50	3.23—4.89	7.6	—
10.....	5.19	6.34	6.30—8.20	12.1	—
20.....	—	11.80	11.58—13.65	18.9	19.0
30.....	—	19.90	—	29.1	30.5
40.....	—	34.0	—	44.1	45.5
50.....	—	56.2	—	66.0	72.0
60.....	—	88.3	—	97.4	107.3
70.....	—	137.1	—	142.0	155.2
80.....	—	202.0	—	204.3	232.9
90.....	—	292.8	—	290.6	346.7
100.....	—	416.5	—	408.5	473.0
110.....	—	582.6	—	—	—

Results are also given by Bineau: at 15°, 7.70 mm.; at 22°, 14.5 mm.; at 32°, 23 mm.; and by Naumann (*Annalen*, 155, 325) at 78°, 185 mm.

In conclusion, it may be pointed out that the correct boiling point of a liquid at atmospheric pressure is best determined by wrapping cotton-wool, or if the liquid attacks that substance, asbestos, round the bulb of the thermometer. By this plan, even though the vapour may be superheated, yet the liquid in contact with the thermometer bulb must be at the true boiling point, since it has a free surface of evaporation. It is to be hoped that future experimenters will adopt this method, for little confidence is to be placed in the results obtained in the usual way.

V.—On the Application of Iron Sulphate in Agriculture, and its Value as a Plant-food.

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IN this paper, details are given of some of my most recent work on the use of ferrous sulphate as a manure. This year, I have grown leguminous, root, and cereal crops with and without an iron manure. The experimental plots of land were (as in the experiments last year) in the vicinity of Bromsgrove, Worcestershire. The soil consists chiefly of clay and loam derived from the Lias, or the upper members of the New Red Sandstone formations, and in a former paper, "Experimental Investigations on the Value of Iron Sulphate as a Manure for Certain Crops," (this Journal, Trans., 1884, p. 71), analyses of this soil are given.

This year, six plots of well-drained land were chosen all about the same area. On plots Nos. I and II, the experiments performed last year on a leguminous crop (beans) were repeated. Plot No. I was manured with crystallised ferrous sulphate of commerce (the quantity applied being $\frac{1}{2}$ cwt. to the acre). Plot No. II was left in its normal condition. As in former experiments, the same number of *bean seeds* were planted on the same day, on each plot of land. At the end of the season the yield of each plot of land was as follows:—

TABLE I.

	Plot of land (manured with FeSO_4).		Plot of land (normal).	
	(1.) Weight when gathered.	(2.) Weight when dry.	(1.) Weight when gathered.	(2.) Weight when dry.
Total weight of crop (grain + straw)	6215 lbs.	5325 lbs.	4793 lbs.	4105 lbs.

The crop of beans (*Vicia faba*) grown by the aid of the iron manure yielded 44 bushels of grain, whilst the crop grown without the iron manure yielded only 28 bushels, so again there is a marked difference in the weight of the produce of the two plots of land. Last year (*loc. cit.*), the iron manure gave an increase of 21 bushels of beans, and now there is an increase of 16 bushels.

TABLE II.—*Analyses of Ashes of Entire Plants.*

	Plants grown with iron manure.	Plants grown without iron manure.
<i>Iron oxide</i> , Fe_2O_3	4·910	1·002
Potash, K_2O	17·965	20·984
Soda, Na_2O	18·021	18·213
Lime, CaO	5·999	7·125
Magnesia, MgO	8·002	8·839
Silica, SiO_2	1·734	2·836
<i>Phosphoric oxide</i> , P_2O_5	40·831	37·814
Sulphuric oxide, SO_3	1·162	1·396
Sodium chloride.....	1·376	1·790
	100·000	99·999

TABLE III.—*Analyses of Ashes of Pods minus the Seeds.*

	Grown with iron manure.	Grown without iron manure.
<i>Iron oxide</i> , Fe_2O_3	2·094	0·924
Potash, K_2O	40·999	42·332
Soda, Na_2O	2·986	3·715
Lime, CaO	7·001	6·548
Magnesia, MgO	7·142	7·231
Silica, SiO_2	0·552	0·525
<i>Phosphoric oxide</i> , P_2O_5	36·235	34·400
Sulphuric oxide, SO_3	2·582	3·442
Chlorine.....	0·407	0·883
	99·998	100·000

TABLE IV.—*Analyses of Ashes of the Seeds.*

	With iron manure.	Without iron manure.
<i>Iron oxide</i> , Fe_2O_3	0·575	0·574
Potash, K_2O	42·502	42·498
Soda, Na_2O	1·362	1·365
Lime, CaO	4·783	4·779
Magnesia, MgO	7·111	7·124
Silica, SiO_2	0·800	0·810
<i>Phosphoric oxide</i> , P_2O_5	38·799	38·800
Sulphuric oxide, SO_3	2·546	2·531
Chlorine.....	1·511	1·519
	99·989	100·000

The analyses were performed in duplicate.

From the tables (pp. 46, 47), it will be seen that the crop of beans was greatly increased by manuring the land with iron sulphate; in fact as much as 1422 lbs. when gathered, and 1220 lbs. when dry, also with an increase of 16 bushels of grain. Comparing them with the results obtained last year, the analyses of the ashes of the various parts of the plant agree very remarkably. Last year an increase of 1573 lbs. was obtained with the iron manure when the crop was gathered, and 1395 lbs. when dry, and an increase of 21 bushels of grain over the crops grown without the iron manure. From last year's analyses and in those given in the present paper, it will be seen that the percentage of ferric oxide in the ashes of the various parts of the plant is much larger when the plants have been grown with ferrous sulphate than without it; and also that the phosphoric oxide in the ash increases as the ferric oxide increases. In Table IV, which is the result of the analyses of the ashes of the seeds, it is plain that there is no difference whether the crop is grown with or without an iron manure. Thus confirming for a second time on a large scale that the ash of the seed or embryo of a plant is very constant in its composition whatever manure is applied to the land.

The next two tables illustrate the percentage of Fe_2O_3 and P_2O_5 in the ashes of the two seasons' crops.

TABLE V.—*Entire Plant.*

	1883.			1884.		
	<i>With iron manure.</i>	<i>Without iron manure</i>	<i>Difference</i>	<i>With iron manure</i>	<i>Without iron manure.</i>	<i>Difference.</i>
Fe_2O_3	4·221	1·063	3·158	4·910	1·002	3·908
P_2O_5	41·902	37·941	3·961	40·831	37·814	3·017

TABLE VI.—*Pods minus Seeds.*

	1883.			1884.		
	<i>With iron manure.</i>	<i>Without iron manure.</i>	<i>Difference.</i>	<i>With iron manure.</i>	<i>Without iron manure.</i>	<i>Difference.</i>
Fe_2O_3	2·021	0·911	1·110	2·094	0·924	1·170
P_2O_5	36·061	34·240	1·821	36·235	34·400	1·835

From the above, it is evident that there is an increase of about 3 per cent. of ferric oxide and phosphoric oxide in the ashes of the entire plant, when grown in a soil containing an iron manure; and an increase of about 1 per cent. of ferric oxide, and nearly 2 per cent. of phosphoric oxide in the ashes of the pods.

I am fully convinced that the proposition I advocated nearly two years ago (*Chem. News*, 47, 27), that a "fairly large proportion of soluble iron in a soil is favourable to the growth of plants developing a large amount of chlorophyll," is a proved fact; and this has been confirmed by all my subsequent researches, and by the recent determinations of chlorophyll which Dr. W. J. Russell has performed on plants grown with and without an iron manure.

I shall refer again to Dr. Russell's experiments in the latter part of this paper.

Cereal Crops.

The next crop to be considered is the cereal. As in the experiments with beans, these wheat crops were grown on well-drained land and under like conditions as to sunshine and rainfall. Of two plots each of the same area, one was manured with iron sulphate ($\frac{1}{2}$ cwt. to the acre) and the other was left in a normal condition.

At the end of the season, the yield of each plot was as follows:—

TABLE VII.

	Plot of land manured with FeSO_4 .		Plot of land (normal).	
	(1.) Weight when gathered.	(2.) Weight when dry.	(1.) Weight when gathered.	(2.) Weight when dry.
Total weight of crop (grain + straw)	5021 lbs.	4301 lbs.	5030 lbs.	4360 lbs.

The crop of wheat grown by the aid of the iron manure yielded 28 bushels of grain, whilst the crop grown without the aid of the iron manure yielded 27 bushels of grain.

From these investigations, an iron manure does *not* appear to be of so great a value as a plant-food in the case of the cereal as in the leguminous crop; for the yield is much the same whether an iron manure is used or not. But there is one well ascertained fact in favour of the use of ferrous sulphate for wheat crops, and that is, the plants

were healthier and completely resisted the attack of the wheat mildew ("rust"): whilst the other crop not manured with iron was attacked to a certain extent; and this may account for the increase of 1 bushel of grain over the crop grown on the normal plot of land.

As in the experiments with the leguminous crop, analyses (in duplicate) of the ashes of the various parts of the plants of each plot of land were made, with the following results:—

TABLE VIII.—*Analyses of Ashes of Entire Plant.*

	Grown with iron manure.	Grown without iron manure.
<i>Iron oxide, Fe₂O₃</i>	2·521	2·0·0
<i>Potash, K₂O</i>	12·024	12·561
<i>Soda, Na₂O</i>	2·135	2·410
<i>Lime, CaO</i>	3·634	3·710
<i>Magnesia, MgO</i>	5·412	5·334
<i>Silica, SiO₂</i>	64·846	61·724
<i>Phosphoric oxide, P₂O₅</i>	4·424	4·524
<i>Sulphuric oxide, SO₃</i>	4·511	4·222
<i>Chlorine</i>	0·493	0·514
	100·000	99·999

TABLE IX.—*Analyses of Ashes of Seeds.*

	Grown with iron manure.	Grown without iron manure.
<i>Iron oxide, Fe₂O₃</i>	1·142	1·124
<i>Potash, K₂O</i>	31·024	32·392
<i>Soda, Na₂O</i>	2·504	2·497
<i>Lime, CaO</i>	10·503	10·668
<i>Magnesia, MgO</i>	3·676	3·784
<i>Silica, SiO₂</i>	1·937	1·964
<i>Phosphoric oxide, P₂O₅</i>	46·222	45·269
<i>Sulphuric oxide, SO₃</i>	1·300	1·294
<i>Chlorine</i>	0·692	1·007
	100·000	99·999

The leaves of the wheat gave 3·814 per cent. of ferric oxide when the crop had been grown with iron, and only 1·642 per cent. when not so treated.

The ash analyses in the case of the *entire* wheat plant show that there is an increase of about $\frac{1}{2}$ per cent. of ferric oxide in the plants manured with iron; but this is all that can be said, and the phosphoric oxide is increased by nearly 1 per cent.

Root Crops.

As before, two plots of land were chosen; one was manured with iron sulphate ($\frac{1}{2}$ cwt. to the acre) and the other was left normal. On these two plots of land, turnips were grown; the yield of each plot was as follows:—

TABLE X.

	Plot of land manured with FeSO_4 .	Plot of land normal.
	Weight when gathered.	Weight when gathered.
Total weight of crop (root + leaves)	50,104 lbs.	44,216 lbs.

The plot of land manured with ferrous sulphate gave $16\frac{1}{2}$ tons, whilst the plot of land in its normal state gave only 13 tons of turnip roots. It is evident that there is a great increase in the produce by manuring the land with iron sulphate.

The next two tables give the analyses of the ashes of this root-crop.

TABLE XI.—*Analyses of Ashes of Turnip Roots.*

	Grown with iron manure.	Grown without iron manure.
<i>Iron oxide, Fe_2O_3</i>	1·210	0·321
<i>Potash, K_2O</i>	43·843	50·124
<i>Soda, Na_2O</i>	3·862	3·621
<i>Lime, CaO</i>	12·962	13·024
<i>Magnesia, MgO</i>	1·900	2·000
<i>Silica, SiO_2</i>	0·816	1·215
<i>Phosphoric oxide, P_2O_5</i>	17·910	16·412
<i>Sulphuric oxide, SO_2</i>	5·010	6·954
<i>Chlorine</i>	3·487	6·328
	100·000	99·999

The analyses in XI and XII (which were done in duplicate) show that there is an increase of nearly four times the amount of ferric oxide in the turnip roots grown with the iron manure over those grown without it; and in the turnip leaves there is more than three times the per-

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centage of ferric oxide in the ashes of the crop grown with iron as compared with that grown without iron.

TABLE XII.—*Analyses of Ash of Turnip Leaves.*

	Grown with iron manure.	Grown without iron manure.
<i>Iron oxide, Fe₂O₃</i>	3·202	0·986
<i>Potash, K₂O</i>	26·124	27·921
<i>Soda, Na₂O</i>	6·210	7·024
<i>Lime, CaO</i>	34·452	35·620
<i>Magnesia, MgO</i>	2·541	4·199
<i>Silica, SiO₂</i>	1·462	2·134
<i>Phosphoric oxide, P₂O₅</i>	6·943	4·218
<i>Sulphuric oxide, SO₂</i>	13·910	11·999
<i>Chlorine</i>	5·154	5·898
	99·998	99·999

Nitrogen in the Crops.

The next set of three tables gives my determinations of the *percentage* of nitrogen in each crop.

TABLE XIII.—*Nitrogen in Beans (Vicia faba).*

	Grown with iron manure.	Grown without iron manure.
<i>Grain</i>	4·920	4·869
<i>Straw</i>	2·188	1·198
	7·108	6·067

TABLE XIV.—*Nitrogen in Wheat (Triticum vulgare).*

	Grown with iron manure.	Grown without iron manure.
<i>Grain</i>	1·809	1·802
<i>Chaff</i>	0·820	0·821
<i>Straw</i>	0·674	0·363
	3·303	2·986

TABLE XV.—*Nitrogen in Turnips (Brassica rapa).*

	Grown with iron manure.	Grown without iron manure.
Root	2·189	2·181
Leaf	4·280	3·265
	6·469	6·446

I have also estimated the *percentage* of soluble carbohydrates (soluble in dilute acids), woody fibre (insoluble in dilute acids), and fat. Table XVI details the results.

TABLE XVI.

	Plants grown with iron manure.				
	Beans.	Bean straw.	Wheat.	Wheat straw.	Turnip.
Soluble carbohydrates..	55·81	44·23	72·14	36·00	8·97
Woody fibre.....	10·21	39·91	5·53	49·25	2·54
Fat.....	2·94	1·82	3·41	2·09	0·81

	Plants grown without iron manure.				
	Beans.	Bean straw.	Wheat.	Wheat straw.	Turnip.
Soluble carbohydrates..	49·32	38·24	66·21	31·95	6·29
Woody fibre.....	7·93	33·67	2·98	43·69	1·45
Fat.....	1·65	1·03	1·32	1·48	0·32

The above table shows that the carbohydrates, woody fibre, and fat are all more or less increased when the plants have been grown by the aid of ferrous sulphate.

The next table gives the determinations by Dr. W. J. Russell of the *relative* amounts of chlorophyll in samples of the leaves from each of my crops. He has kindly determined the relative amounts in equal weights and in equal areas of each sample, with the following results:—

TABLE XVII.—*Dr. Russell's Estimation of the Relative Amount of Chlorophyll in the Leaves.*

No. of Sample.	Leaves.	In equal areas.	In equal weights.
1	Beans (grown with FeSO_4)	100	100
2	Beans (" without FeSO_4)	79	76
1	Turnip (grown with FeSO_4)	59	61
2	Turnip (" without FeSO_4)	40	39
1	Wheat (" with ")	115	72
2	Wheat (" without ")	100	81

The leaves were collected on the same day, and were of the same age in each case. From the above determinations, it is evident that iron nourishes the chlorophyll granules, a proposition I advanced some few years ago. From Dr. Russell's analyses, it will be seen that in each plant—with the exception of wheat—when the plants have been grown with an iron manure, the chlorophyll in "equal areas" and in "equal weights" has been greatly increased. And now comes the question, what has increased the chlorophyll? The iron, because it nourishes the granules, and always is to be found near to the granules themselves in the crystallised condition when sections of the leaves are examined microscopically. (See my paper, *Chem. Soc. J. Trans.*, 1883, p. 195.)

General Conclusions.

My enquiries on this subject have led me to the following conclusions as to the effect of ferrous sulphate as a plant-food:—

I. In the case of those plants which develop a large amount of chlorophyll, for examples, beans, cabbages, and turnips, an iron manure is most beneficial, considerably increasing the harvest. (See the present paper and *Trans.*, 1884, pp. 71—75; *Chem. News*, 47, 27—78.)

II. An iron manure greatly increases the percentage of soluble carbohydrates, woody fibre, and fat in certain plants, this, of course, being an outcome of the increase in the amount of chlorophyll in the leaf; for the chlorophyll forms starch, which is converted into "carbohydrates," cellulose, &c. (See the present paper.)

III. I have found monoclinic crystals of ferrous sulphate near to the chlorophyll granules when sections of the leaves are examined under the highest powers of the microscope, the crystals being tested chemically and proved to be ferrous sulphate. (See *Trans.*, 1883, pp. 125—197; also *Journal Royal Microscopical Society*, 1883, p. 536.)

IV. That in certain cases the phosphoric oxide in the ashes of plants grown with this new manure increases as the ferric oxide increases. (See present paper; also *Trans.*, 1884, pp. 71—75; *Chem. News*, 47, 27—28.)

V. That ferrous sulphate is a good plant-food, proved by the increase in the harvest as shown above; yet in *excess* it acts as a poison to plant-life, a solution containing $\frac{1}{4}$ per cent. of FeSO_4 being fatal to most plants; and when the amount of *ferric oxide* in the ash of all the plants examined was 10 per cent. the plant previously died. (See *Chem. News*, 50, 167; *Chemiker-Zeitung*, 1884, p. 757; and *Chem. News*, 50, 193.)

VI. The sulphur of the ferrous sulphate acts as a food for the protoplasm of the cell, and the iron for the chlorophyll itself. (See *Chem. News*, 49, 237, 265; 50, 32; also *Chemiker-Zeitung*, 1884, p. 863; this *Journal*, *Abstr.*, 1884, p. 848.)

VII. The nitrogen in the plants grown with ferrous sulphate is to some extent increased. (See present paper.)

VIII. Iron sulphate increases the amount of chlorophyll in the leaf. (See Dr. Russell's estimations in present paper.)

IX. Iron sulphate acts in the soil as an antiseptic agent, destroying to some extent certain parasitic diseases which attack our crops. (See *Chem. News*, 49, 279; *Abstr.*, 1884, p. 1070.)

X. My experiments have also led me to conclude that the most active rays of white light for *root-absorption* are between Fraunhofer's lines D and E. (See *Trans.*, 1884, pp. 74—75.)

In conclusion, I wish to tender my best thanks to Dr. W. J. Russell, F.R.S., for his determinations of the relative amounts of chlorophyll in the plants. I also wish to thank Dr. T. L. Phipson, F.C.S., and my friends Mr. T. P. Wright, Dr. J. Johnstone, M. E. C. Conrad, F.C.S., of Bordeaux, and Mr. E. L. Rhead (Demonstrator in Chemistry, Technical College, Manchester), for many kind suggestions.

VI.—Action of the Halogens on the Salts of Trimethylsulphine.

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I. Action of Iodine on the Haloid Salts.

WHEN dry trimethylsulphine iodide is shaken up with an ethereal solution of iodine, it becomes converted into a heavy black tarry liquid, which smells strongly of iodine; this is easily soluble in alcohol, and it reappears unchanged when the solution is evaporated. It decomposes slowly when warmed with water, iodine being evolved. It was not found possible to obtain the substance in a state fit for analysis, but there is no doubt that it is of the order of the so-called polyiodides. Jørgensen (*J. pr. Chem.*, **3**, 338) obtained a similar compound of triethylsulphine, which gave a crystalline double salt with mercuric iodide.

The bromide and the chloride of trimethylsulphine behave in a similar manner; but, if the tarry product is washed with ether and dissolved in alcohol, large reddish-black crystals are obtained when the solution is evaporated over sulphuric acid. These crystals smell of iodine and are not stable in the air. In these circumstances, it was not thought worth while to analyse them, but their general resemblance to the more stable compounds described below leaves no doubt in our minds that they consist respectively of the *bromo-diiodide* and the *chloro-diiodide* of trimethylsulphine,— Me_3SBrI_2 and Me_3SClI_2 . A compound in all respects similar to, and probably identical with, the second of these, is obtained by acting on trimethylsulphine iodide with iodine monochloride.

II. Action of Bromine on the Iodide.

When bromine vapour is poured over dry trimethylsulphine iodide, much heat is developed and the colourless crystals melt to a dark red liquid. The reaction goes more quickly, and, in fact, with violence, if the bromine is added in the liquid state. When addition of bromine produces no further action, the heavy red oil is exposed for a short time to the air, whereby it loses most of the excess of bromine and becomes solid. The mass is then broken up, shaken two or three times with a little ether, to remove the last traces of bromine, and dissolved in sufficient hot alcohol; as the solution cools, an abundant crop of brilliant orange-red crystals is deposited. The mother-liquor

gives a further but smaller yield when allowed to evaporate in a vacuum; these crystals are of a somewhat darker shade in colour than the others, although of the same composition. The total yield approaches very nearly to that indicated by theory.

Analysis shows the compound to be *trimethylsulphine dibromiodide*, Me_3SIBr_2 . The sulphur was estimated by combustion with a mixture of five parts of potassium carbonate to one of potassium chlorate,—a method we would recommend for those cases where the sulphur is combined directly with methyl, &c. The halogens were estimated in solutions obtained by decomposing the salt with dilute sulphurous acid: in one, the bromine was determined after removing the iodine with cupric sulphate; in the other, the total halogen was determined as silver salt.

I.	0.2625 gram	gave 0.0946 gram CO_2 and 0.0623 gram H_2O .
II.	0.2564	„ 0.0944 gram CO_2 and 0.0605 gram H_2O .
III.	0.2329	„ 0.1421 gram BaSO_4 .
IV.	0.2258	„ 0.2330 gram AgBr .
V.	0.1073	„ 0.1797 gram mixed AgBr and AgI .

	Calculated.	Found.				
		I.	II.	III.	IV.	V.
C_3	9.87	9.83	10.04	—	—	—
H_9	2.47	2.63	2.62	—	—	—
S	8.79	—	—	8.88	—	—
I	34.89	—	—	—	—	34.74
Br_2	43.96	—	—	—	43.90	—
	100.0	—	—	—	—	—

Properties of Trimethylsulphine Dibromiodide.—The orange-red crystals are not deliquescent, and are perfectly stable in air. When heated, they melt at 94 – 95° , with partial decomposition. A brown oily distillate passes over at higher temperatures and, finally, at about 180° , methyl sulphide and iodine vapour. The crystals are somewhat soluble in cold alcohol or ether, and much more so in hot alcohol. The alcoholic solution seems to undergo slight decomposition on long standing. The reaction with water is very characteristic; for the crystals, when shaken with it, with or without the application of heat, quickly melt to a black oil, which resembles the periodide in appearance. On long boiling, it dissolves in the water, iodine being evolved. *Platinic chloride*, added to the alcoholic solution, produces a bulky flesh-coloured precipitate.

This is soluble in hot water, from which it crystallises in the golden cubes and octahedra characteristic of trimethylsulphine platinum-chloride. Estimations of the platinum confirmed its identity.

- I. 0.2377 gram of the salt gave 0.0824 gram of platinum.
 II. 0.2436 " " 0.0843 " "

Pt per cent.	Calculated for (Me ₃ S) ₂ PtCl ₆ .	Found.	
		I.	II.
.....	34.94	34.66	34.60

Freshly precipitated *silver oxide*, when shaken with the alcoholic solution, is converted into haloid salt, the liquid at the same time losing its orange colour and acquiring an alkaline reaction. This is due to the formation of trimethylsulphine hydroxide. On evaporation, some crystals of iodoform are obtained. *Silver nitrate* and *silver sulphate* also decolorise the alcoholic solution, rendering it strongly acid. The corresponding salts of trimethylsulphine are probably produced, but the reactions have not been fully investigated. *Alcoholic potash*, added to the alcoholic solution till the colour is gone, gives a yellow precipitate which increases on the addition of water, and is proved to be iodoform by its smell and general properties. The filtrate from this contains haloid salts of potassium and trimethylsulphine. The final action of *aqueous potash* on the crystals themselves is the same, except that no iodoform is produced; but there seems to be at first an unstable product formed which imparts an opalescent green colour to the solution. *Ammonia solution* at once converts the crystals of the dibromiodide into a black solid matter which, after careful washing and drying, has the appearance and properties of iodide of nitrogen, exploding with great violence and extreme readiness. The filtrate contains haloid salts of ammonium and trimethylsulphine.

Ammonia gas acts quite differently. If the gas be blown from the mouth of a bottle of ammonia solution over the orange-red crystals, these at once acquire a dark green colour which, however, the warmth of the hand is sufficient to dispel. But if the crystals be submitted to a current of dry ammonia, this initial green colour quickly gives place to black, which is in turn succeeded, in the course of two hours or more, by a uniform light apple-green. These phenomena are due to the formation of a direct addition product of the composition Me₃SIBr₂.2NH₃. It is an amorphous, non-explosive, light-green solid body, stable only in an atmosphere of ammonia. In a current of dry air, it loses ammonia and reverts to the intermediate black condition, the loss being very rapid at first, then slower and slower,

though it probably becomes complete in the course of time. At a temperature of $75-80^{\circ}$ the compound melts, ammonia is rapidly evolved, and the original dibromiodide is left. Mere solution in alcohol effects a similar decomposition. Water dissolves it with liberation of iodine, which explains the formation of iodide of nitrogen by the action of excess of ammonia solution on the dibromiodide.

The composition of this very unstable compound could be determined only synthetically. It was done in the following manner. The powdered dibromiodide was placed in a porcelain boat inside a short glass-stoppered tube, the weight of the tube and boat together being known, as well as that of the substance taken. The tube was then clamped in a horizontal position, and closed with a cork through which passed two tubes—one for outlet and the other, reaching to the far end, for inlet of the ammonia. The gas, dried by passing through U-tubes containing solid potash, was then allowed to act for a quarter of an hour, at the end of which time it was displaced for a few seconds by dry air, and, the cork having been quickly exchanged for the glass stopper, the tube was weighed.

This operation was repeated several times, until the weight became constant. While weighing—though this was done as quickly as possible—the light green colour became tarnished with black at the edges.

0.7172 gram of the dibromiodide became 0.7841 gram by absorption of ammonia.

	Gain per cent.
Calculated for $\text{Me}_3\text{SIBr}_2, 2\text{NH}_3$	9.34
Found	9.32

III. Action of Chlorine on the Iodide.

Chlorine, well washed and dried, is passed into a flask containing dry powdered trimethylsulphine iodide. This at once melts, much heat being developed, and a pasty black substance is formed, which quickly changes to a light yellow solid body. If the flask be surrounded with cold water, the product will remain of a dark colour, for the reaction is checked at the first stage; but it may be completed by afterwards substituting warm water for the cold and continuing the passage of the chlorine. The final product consists of *trimethylsulphine dichloriodide*, Me_3SICl_2 . It is readily purified in the same manner as the dibromiodide, and separates from the hot alcoholic solution in an abundant crop of canary-yellow crystals, which closely resemble the dibromiodide in general properties. The mother-liquor, when evaporated in a vacuum, yields a smaller crop of crystals, of a darker shade, but identical composition. On long standing, the alco-

holic solution undergoes some decomposition, distinctly more than in the case of the dibromiodide.

Analysis.—I. 0.1953 gram of the substance gave 0.0931 gram CO_2 and 0.0582 gram H_2O .

II. 0.1847 gram gave 0.0892 gram CO_2 and 0.0565 gram H_2O .

III. 0.2321 ,, 0.1959 ,, BaSO_4 .

	Calculated.	Found.		
		I.	II.	III.
C ₃	13.09	13.05	13.17	—
H ₉	3.27	3.31	3.40	—
S.....	11.63	—	—	11.59
I.....	46.18	—	—	—
Cl ₂	25.83	—	—	—
	100.00	—	—	—

Properties.—The yellow crystals of the dichloriodide are stable in air at ordinary temperatures. They melt at 103–104° with partial decomposition, evolve a brown oily distillate when further heated, and the vapours of methyl sulphide and iodine above 170°. *Platinic chloride*, added to the alcoholic solution, gives a bulky precipitate, shown to consist of trimethylsulphine platinochloride by its general properties and by the following analyses:—

I. 0.1176 gram gave 0.0404 gram of platinum.

II. 0.1621 ,, 0.2458 ,, AgCl.

	Calculated for (Me ₃ S) ₂ PtCl ₆ .	Found.
Pt	34.94	(I.) 34.35
Cl	37.71	(II.) 37.51

With *silver salts* and with *caustic potash*, the dichloriodide acts in a manner precisely similar to the dibromiodide. *Ammonia solution* decomposes it with formation of iodide of nitrogen. With perfectly dry *ammonia gas*, it forms the compound $\text{Me}_3\text{SiCl}_2 \cdot 2\text{NH}_3$, the various stages in the reaction being hardly distinguishable from those in the formation of the corresponding dibromiodide derivative. The final product, however, is not so light in colour; and, when exposed to the atmosphere, it not only loses ammonia but absorbs moisture, and becomes converted into a wet black paste, which is not the case with its analogue. In other respects it resembles it closely. The composition was determined synthetically in the manner already described.

0.2738 gram of the dichloriodide became 0.3067 gram by absorption of ammonia :—

	Gain per cent.
Calculated for $\text{Me}_3\text{SiCl}_2, 2\text{NH}_3$	12.36
Found	12.02

IV. Action of Iodine Monochloride on the Chloride.

This results, as might be expected, in the formation of *trimethylsulphine dichloriodide*. The reaction which takes place when the iodine monochloride is poured gradually over the dry chloride closely resembles that produced by the action of bromine on the iodide. Much heat is developed, and the salt melts to a black pasty mass. This, however, assumes a light yellow colour and dry consistency when purified by a few washings with ether. The crystals obtained by cooling the hot alcoholic solution are identical in appearance and properties with those of the dichloriodide obtained by the method already described. The yield is large.

V. Action of Iodine Monochloride on the Bromide.

This action produces a body which, after washing with ether, separates from hot alcohol in the form of crystals, which are intermediate in colour between the light yellow dichloriodide and the orange-red dibromiodide, both of which it otherwise closely resembles. It melts at 87° with partial decomposition, which becomes complete at 180 – 190° .

Combustions of the substance gave the following results, showing that it consists of *trimethylsulphine chlorobromiodide*, Me_3SiBrCl .

- I. 0.3071 gram substance gave 0.1314 gram CO_2 and 0.0832 gram H_2O .
- II. 0.3228 gram substance gave 0.1378 gram CO_2 and 0.0894 gram H_2O .

	Calculated for Me_3SiBrCl .	Found.	
		I.	II.
• C	11.27	11.67	11.64
H	2.82	3.01	3.07

VI. Action of Bromine on the Bromide.

This action resembles that of bromine on the iodide, but the properties of the products of the two reactions are quite different. Heat is evolved, and the crystals melt to a dark-red heavy liquid, which does not solidify when washed with ether; nor can it be crystallised

from alcohol, as it separates unchanged in appearance when the solution is evaporated. When surrounded with a freezing mixture of snow and salt, it becomes more viscous but does not solidify. It smells of bromine; and it is slowly decomposed on exposure to the atmosphere, drops of a solution of trimethylsulphine bromide (which is deliquescent) making their appearance on the surface of the liquid after a day or two. It is decomposed much more quickly when heated on the water-bath, and the bromide is then obtained in the crystalline state. Even when the substance is kept in a desiccator containing sulphuric acid, there is continuous, though slow, loss of bromine. When shaken with water, it is slowly decomposed and passes into solution.

As such a body could not be obtained in a state fit for analysis, it was thought desirable to make some quantitative synthetic experiments with perfectly dry materials. The purity of the trimethylsulphine bromide was first ascertained by an estimation of its bromine. 0.2260 gram of the salt gave 0.2695 gram AgBr.

	Calculated.	Found.
Br.	50.95	50.74

In this and subsequent experiments with the bromide and chloride, which are both extremely deliquescent, special precautions were employed to obtain the salt in a perfectly dry state. It was placed in a small porcelain boat inside a glass tube, the boat and tube, with a ground glass stopper, being previously weighed. The tube was then placed horizontally, without its stopper, in a larger tube surrounded with boiling water, and closed by a doubly perforated cork. The salt being thus kept at 100°, dry air was led over its surface for from two to three hours. The tube was then quickly stoppered and weighed with its contents. By replacing the glass stopper by a cork provided with inlet and outlet tubes, it was possible afterwards to operate on the weighed salt with a stream of chlorine, or of air charged with bromine vapour, and to weigh the product (after clearing the tube out with dry air) without more than a momentary exposure to the atmosphere.

0.2441 gram of the dry bromide was exposed for two hours to a perfectly dry current of air charged with bromine vapour. The red oil, which was rapidly formed, continued during that time to increase in volume, in depth of colour, and in mobility. The increase in weight was 1.3208 gram, which is equivalent to a gain of from ten to eleven atoms of bromine by one molecule of the bromide; and there is no reason to suppose that the absorption would have stopped there. Dry air was then passed over the surface of the liquid for several hours, and weighings were made at intervals; after which the tube

and its contents were left for three days in a desiccator containing solid potash and then again weighed. The following table shows the results of this experiment:—

	Air passed.	Weight.	Weight gained.	Gain per cent.	Mols. of Br gained by 1 mol. of Me_3SBr .
Taken, 0.2441 gram of Me_3SBr , and bromine passed over it for two hours.	—	1.5649	1.3208	541	5.30
	2 hours ...	0.7510	0.5069	207	2.03
	4 „ ...	0.5483	0.3042	124	1.22
	6 „ ...	0.5031	0.2590	106	1.04
	8 „ ...	0.4777	0.2336	95	0.93
	9 „ ...	0.4689	0.2248	92	0.90
	11 „ ...	0.4613	0.2172	89	0.87
	After 3 days over KOH	0.4467	0.2026	83	0.81

Now, the calculated percentage gain, for the formation of Me_3SBr_3 , is 101.9, so that it is obvious that this compound, if formed at all, tends, on the one hand, to absorb a large excess of bromine when in an atmosphere containing it, and, on the other, to decompose steadily when in air free from bromine. As it is impossible, however, to isolate this or any other definite compound, all we can assert, is that bromine does combine with trimethylsulphine bromide with development of heat, and that the analogy of the dibromiodide is in favour of the supposition that the tribromide is formed.

VII. Action of Bromine on the Chloride.

This action is precisely similar in character and appearance to that of bromine on the bromide. A dark-red oil is rapidly formed, which goes on absorbing bromine as long as it is exposed to air charged with the vapour of that substance, but gives it up again, at a progressively decreasing rate, in a current of dry air or in a desiccator containing solid potash. It is unnecessary to give the details of the experiments, as they were similar to the one described in the last paragraph: they afforded no evidence in favour of the existence of the chlorodibromide, $\text{Me}_3\text{SBr}_2\text{Cl}$, or of that of any other definite compound.

VIII. *Action of Chlorine on the Bromide.*

At the first touch of chlorine, the colourless crystals of trimethylsulphine bromide assume an orange tinge; and then they gradually melt to a clear yellow viscous liquid, in which, at first, solid orange-coloured pieces may be seen floating. The final product smells of chlorine, which it evolves when exposed over solid potash or subjected to a current of dry air. Water acts on it, causing the liberation of minute bubbles of chlorine. The following quantitative experiment was made.

0.2746 gram of the dry bromide was subjected to the action of dry chlorine for one hour, at the end of which time it was found to weigh 0.4100 gram. A second hour's chlorination increased this to 0.4169 gram; and it did not increase further. This is equivalent to a gain of 51.8 per cent., or 1.146 molecules of chlorine by one molecule of the bromide, the formation of $\text{Me}_3\text{SBrCl}_2$ requiring a percentage gain of 45.2. The product was then allowed to stand for two days over solid potash, after which the weight was found to be 0.3873 gram, which corresponds to a gain of 41.0 per cent., or 0.907 molecule of chlorine by one molecule of the bromide. On further exposure it continued to lose weight, though slowly.

The experimental evidence in this case, therefore, decidedly favours the belief that *trimethylsulphine dichlorobromide*, $\text{Me}_3\text{SBrCl}_2$, is formed, which is what one would expect from the analogy of the dichloriodide. No doubt, the very different physical properties of chlorine and bromine may account for the fact that trimethylsulphine bromide (and, as will be seen, chloride) absorbs but a small excess of the former, though an apparently unlimited excess of the latter.

IX. *Action of Chlorine on the Chloride.*

In order to observe this action properly, it is necessary to have both the chlorine and the chloride absolutely dry. If this precaution be taken, the crystals will turn yellow and begin to melt the instant the chlorine touches them. There is no sensible development of heat. After a few minutes the whole mass becomes converted into a clear pale yellow liquid, which undergoes no further change of appearance, though it goes on absorbing chlorine for some few minutes longer. This product has some characteristic properties. When exposed to the air for a very brief period, it suddenly solidifies; and when once this (apparently physical) change has taken place, the substance is not in the least affected by subsequent exposure to a chlorine current, however prolonged. Thus, in one experiment, the current of chlorine was stopped as soon as the product appeared to be uniformly liquid (five minutes from commencement), and dry air was then

passed through to sweep out the tube. This caused the substance to solidify. It was weighed and then again exposed to chlorine for half an hour; but the weight was found to be unchanged, though the quantity of chlorine taken up was not nearly so large as in other experiments. In another case, after nearly the maximum amount had been absorbed (twenty minutes from commencement), some accidental cause produced sudden solidification; and the rapid escape of dissolved chlorine caused the formation of a number of small crater-like excrescences on the surface. The action of a drop of water on the solid compound is particularly striking, for it causes a violent effervescence of chlorine. At the same time trimethylsulphine chloride passes into solution. Absolute alcohol and ether both decompose it in a similar manner; but the chlorine is, of course, not liberated as such. The chlorinated chloride is decomposed more rapidly in dry air than any of the other compounds already described.

The purity of the chloride employed in the experiments tabulated below was tested by means of a chlorine estimation. 0·3100 gram of the salt gave 0·3899 gram of AgCl.

	Calculated for Me_3SCl .	Found.
Cl	31·55	31·11

In every experiment, the salt was dried for from two to three hours in the manner already described. In experiment I the tube was swept out with a current of dry air before weighing, so that the product assumed the solid state. In the other cases, this was avoided by weighing the tube full of chlorine (with its cork, and tubes closed by caoutchouc caps); and the weight to be deducted for this extra chlorine was determined as accurately as possible by preliminary experiments. In experiment IV it was proved that the maximum weight had been gained.

No. of experiment.	Weight of chloride taken.	Weight of product.	Gain per cent.	Molecules of Cl gained by Me_3SCl .	Time allowed.
I	0·2770	0·3874	39·85	0·631	5 minutes
II	0·3110	0·5170	66·23	1·019	20 "
III	0·2377	0·4063	71·14	1·127	30 "
IV	0·2344	0·4036	72·18	1·144 (maximum)	45 "

In order to prove beyond doubt that the reaction consists in the simple addition of chlorine, and that there is no substitution of that

element for hydrogen, a combustion of the product of experiment I was made, the results of which may be compared with those obtained from the unacted-on chloride.

I. 0.2634 gram of the unacted-on chloride gave 0.3045 gram CO_2 and 0.1918 gram H_2O .

II. 0.2770 gram of the chloride, after it had been acted on by chlorine, gave 0.3217 gram CO_2 and 0.2020 gram H_2O .

	Calculated for Me_3SCl .	Found.	
		I. Before chlorination.	II. After chlorination.
C	32.00	31.72	31.67
H	8.00	8.14	8.10

From these experiments, it seems fair to conclude that *trimethylsulphine trichloride*, Me_3SCl_3 , is formed—a peculiar and unstable compound possessed of a limited power of dissolving chlorine when placed in an atmosphere of that gas.

X. Action of Halogens on the Sulphate.

We have not yet fully investigated the reactions of trimethylsulphine sulphate with the halogens; but we have ascertained by experiments the following facts. (1.) Iodine does not combine with it in the same way as it does with the haloid salts. (2.) Bromine combines with it to form a red solid body, which resembles the dibromiodide rather than the products obtained by bromination of the bromide and chloride, but is less stable than the former. (3.) Chlorine acts on it to form a product which closely resembles the trichloride in its general properties, and particularly in the rapid effervescence of chlorine which occurs when water is dropped on it. We are pursuing the investigation of these reactions and of those of the halogens with other salts of trimethylsulphine.

XI. Summary and Theoretical Considerations.

It has been shown that all the haloid salts of trimethylsulphine combine directly with chlorine, bromine, iodine, and iodine monochloride. In no case does there occur a replacement of one halogen by the other. The product of each reaction may be formulated as Me_3SX_3 (if we understand X to represent Cl, Br, or I, indiscriminately), this being proved with certainty in some cases, and fairly inferred in those where proof is wanting. In the following table, which shows the ten possible variations of the general formula, a query (?)

indicates that the substance has not been proved by quantitative experiments to have the formula attributed to it. This proof might be obtained in the cases of Nos. II and III; in those of I, VII, and VIII, this is rendered impossible by the readiness with which the compounds dissolve excess of the halogen, and by their unstable nature.

No.	Formula.	Appearance.	Behaviour in dry air.	How produced.
I	Me_3SI_2 ? ..	Black tarry matter.....	—	$\text{Me}_3\text{SI} + \text{I}_2$
II	$\text{Me}_3\text{SI}_2\text{Br}$? ..	Dark crystals	—	$\text{Me}_3\text{SBr} + \text{I}_2$
III	$\text{Me}_3\text{SI}_2\text{Cl}$? ..	Dark crystals	—	$\text{Me}_3\text{SCl} + \text{I}_2$, or $\text{Me}_3\text{SI} + \text{ICl}$
IV	Me_3SIBr_2 ..	Orange-red crystals	Perfectly stable..	$\text{Me}_3\text{SI} + \text{Br}_2$
V	Me_3SIBrCl ..	Orange crystals	Perfectly stable..	$\text{Me}_3\text{SBr} + \text{ICl}$
VI	Me_3SICl_2 ..	Yellow crystals	Stable.....	$\text{Me}_3\text{SI} + \text{Cl}_2$, or $\text{Me}_3\text{SCl} + \text{ICl}$
VII	Me_3SBr_3 ?..	Orange-red viscous liquid	Loses Br slowly..	$\text{Me}_3\text{SBr} + \text{Br}_2$
VIII	$\text{Me}_3\text{SBr}_2\text{Cl}$?	Orange-red viscous liquid	Loses Br slowly..	$\text{Me}_3\text{SCl} + \text{Br}_2$
IX	$\text{Me}_3\text{SBrCl}_2$..	Yellow viscous liquid ...	Loses Cl (and Br?)	$\text{Me}_3\text{SBr} + \text{Cl}_2$
X	Me_3SCl_3 ..	Yellow liquid (or solid) ..	Loses Cl.....	$\text{Me}_3\text{SCl} + \text{Cl}_2$

In this list, it will be seen that those compounds are the most stable which contain one iodine-atom; that those which contain more than one are difficult to purify on account of peculiarities which seem to characterise many of the known polyiodides of organic bases; and that those which contain no iodine tend to break up into their components, except in an atmosphere of chlorine or bromine, as the case may be.

As regards the constitution of these compounds, three theories are worthy of consideration. The first would regard them as examples of mere molecular combination, and would write the general formula $\text{Me}_3\text{SX}, \text{X}_2$. This, however, is not in accordance with the nature of the decomposition which the crystalline members of the series undergo when heated, nor with the fact that so high a temperature is required to effect it. The second theory is represented by the formula $\text{Me}_3\text{S}-\text{X} < \frac{\text{X}}{\text{X}}$, and assumes that the halogen-atom of the original salt becomes triad. In support of this may be quoted the general reactions of the dibromide and the dichloride, and particularly the fact that they combine with two molecules of ammonia; also the ease with which the trichloride breaks up, inasmuch as we should certainly expect the monad group Cl_3 to be very unstable if it exists at all. But this theory obviously cannot account for the combination of trimethylsulphine sulphate with bromine and with chlorine; and this fact must be regarded as affording a strong argument against

the theory; for we have already pointed out the striking similarity between the compounds so formed and some of those derived from the haloid salts.

The third theory is capable of general application to all the bodies we have described. It assumes that they are trimethyl-sulphinic

salts, $\text{Me}_3\text{S} \begin{smallmatrix} \text{X} \\ \diagup \\ \text{X} \\ \diagdown \\ \text{X} \end{smallmatrix}$, in which the sulphur atom is hexad.

The analogy between these bodies and the so-called polyiodides (Weltzien, *Ann. Chem. Pharm.*, **86**, 292; **91**, 36; Tilden, this Journal, 1865, 99; Jörgensen, *Ber.*, **2**, 460; *J. pr. Chem.*, **3**, 145, 328) and polybromides (Marquart, *J. pr. Chem.*, **1**, 429) of the nitrogen bases is well marked. Moreover, Tilden (this Journal, 1866, 145) describes a dichloriodide of tetrethylammonium, which he obtained by acting on the chloride with iodine monochloride; and Weltzien (*Ann. Chem. Pharm.*, **99**, 11) also obtained some similar compounds by indirect means. Professor Crum Brown suggested to us, therefore, that we should investigate the hitherto untried action of bromine on the iodide of tetramethylammonium; and we have found that this reaction produces a red crystalline body so closely resembling the dibromiodide of trimethylsulphine as to leave no doubt of its true nature. Moreover, we have found that both bromine and chlorine unite with the sulphate of tetramethylammonium to form compounds which cannot be distinguished by their general properties from those obtained from the corresponding trimethylsulphine salt. We purpose making a complete investigation of the halogen compounds of the tetramethylammonium salts; but what we have already observed, taken together with the work of those chemists whom we have quoted, seems to justify us in saying that there is a large class of substances formed by the union of halogens with the salts of organic bases; and that any theory, to be acceptable, must be applicable equally to such examples as the "polyiodides," the dibromiodide of trimethylsulphine, the trichloride of trimethylsulphine, the product resulting from the union of bromine with tetramethylammonium iodide, and the products obtained by the union of bromine and chlorine with the sulphates of trimethylsulphine and tetramethylammonium. If, therefore, the bodies we have described are trimethylsulphinic salts, containing hexad sulphur, it would seem that nitrogen is capable of becoming heptad. Further evidence is, however, wanted on this point.

In conclusion, we desire to express our gratitude to Professor Crum Brown for having given us the great benefit of his aid and advice in this investigation.

VII.—*On the Decomposition of Silver Fulminate by Hydrochloric Acid.*

By EDWARD DIVERS, M.D., and MICHITADA KAWAKITA, M.E.

THE Society has received from us a note of the fact that silver fulminate differs from mercury fulminate in yielding much less than the full amount of hydroxyammonium chloride, and in yielding ammonium chloride. The present communication contains the results of our further examination of the action of hydrochloric acid on silver fulminate, and also those of the examination of the action of dilute hydrochloric acid on mercury fulminate, and on fulminates, in relation to the production of hydroxyammonium chloride, formic acid, and ammonia, and of Steiner's production of oxalic acid from mercury fulminate.

The silver fulminate was prepared in small quantities at a time, and was dried, with certain precautions, in an oven at or near 100°. In two preparations we determined the silver as chloride, and found 71.79 and 71.76 per cent., in place of 72.00 as calculated.

Unlike the mercury salt, silver fulminate is energetically attacked by concentrated hydrochloric acid. As mentioned in our paper on mercury fulminate, it is hardly necessary to use Steiner's precaution of working with that salt only when moist; and although the reaction between silver fulminate and the acid is of a kind suggestive of danger, we have used it in the dry state without accident. The concentrated acid, as it comes in contact with the bulky salt, causes it to shrivel up and decompose with a loud hissing noise and development of heat. If the heating is not checked, the silver chloride produced is at first stained orange, but rapidly loses this colour, imparting it to the acid mother-liquor. The heating may be prevented or reduced, both by taking only a small quantity of the fulminate at a time, and by dropping it into a considerable excess of the acid artificially cooled. The colour of the solution disappears during subsequent evaporation.

Besides the colouring matter, there is at first among the products of the reaction an unstable, colourless substance, which gives an intense wine-red colour with ferric chloride, both in the strongest acid solution or in one that has been neutralised. Long standing in the cold or a few minutes' heating, deprives the solution of the power of changing in colour with ferric chloride. This substance is also formed from mercury fulminate, and, as we have already pointed out in our preliminary note, is probably identical with that met with by Gay-Lussac and Liebig in their examination of silver fulminate, and

described by them as a chlorinated acid containing nitrogen, and not precipitable by silver nitrate. This acid, however, is stated by them to have given the red colour only when the solution had been previously neutralised with alkali.

In all cases when silver fulminate is treated with hydrochloric acid, the odour of hydrogen cyanide is perceptible, but more markedly when dilute acid is taken. Two determinations were made of the amount of hydrogen cyanide produced when concentrated hydrochloric acid is used; in one experiment this was found to be 0.29, and in another 0.38 per cent. The determinations were made with care, but the results are to be taken as only approximately accurate, and as serving to show the smallness of the quantities of hydrogen cyanide produced. The procedure was first to let hydrochloric acid through a tap-funnel into a retort containing the dry, weighed fulminate, and connected air-tight with two U-tubes in series containing solution of potassium hydroxide, and, next, slowly to aspirate air through the apparatus for some time, the retort being kept warm. The contents of the receivers were then treated with enough silver nitrate to cause a precipitate, and were filtered. Lastly, the silver in solution in the alkaline liquid was determined and taken, in calculating the hydrogen cyanide, as having existed in the solution as silver potassium cyanide. Liebig's volumetric method could not be employed, because of the presence in the solution along with the cyanide of a minute quantity of some substance sharply reducing silver to the metallic state.

The process of estimating the hydrogen cyanide indicated, therefore, the possibility of the simultaneous generation of a very small quantity of a highly volatile and oxidisable matter. Besides showing this reducing action on silver nitrate, the alkaline solution acquired in some experiments a slight brown colour during the aspiration. Our endeavours to isolate or identify any such substance, or to get uniform indications, were, however, unsuccessful, and we believe now that traces of the contents of the retort must have been carried over mechanically, although unnoticed, by being first thrown up into the head of the retort by the violent action between the acid and the fulminate when they met, and then washed down into the receiver by condensing vapours.

The hissing noise of the decomposition of silver fulminate by hydrochloric acid is connected with a not inconsiderable escape of carbonic anhydride. We have collected this escaping gas by decomposing the fulminate with acid in a tube exhausted of air by the Sprengel pump, and have obtained in this way 4.4 per cent., which is the equivalent of $\frac{1}{3}$ of the total carbon. This quantity is largely in excess of what can possibly be liberated when the fulminate is dropped suddenly into abundance of acid, and its production is due to

the fact that, when working in a vacuum, the acid has to be added to the fulminate, and then meets it in the form of fine streams or jets—a condition of things allowing of great local heating and thus favouring the generation of carbonic anhydride. Working in a retort, filled with air as usual, and adding the whole of the acid to be used suddenly to the fulminate, we have collected the escaping carbonic anhydride in barium hydroxide solution, and thus obtained evidently much less than when working in a vacuum, although as yet we have made no exact measurement of the quantity formed in this way. During the evaporation of the acid solution, a little carbonic anhydride continues to escape from it with the vapour, even after the precaution has been taken to expose it for some time in an open vessel on a water-bath before distilling.

In the decomposition of silver fulminate by hydrochloric acid, there is liberated no gas but carbonic anhydride and hydrogen cyanide, neither nitrogen, nitrous oxide, nitric oxide, nor carbon monoxide.

The yield of hydroxyammonium chloride depends on the strength of the hydrochloric acid used. In decomposing the fulminate, care was taken to minimise the spontaneous heating-up of the mixture. The fulminate was added to moderate excess of the fuming acid in some cases, and in others to large excess. The product was warmed, diluted, well shaken to collect together the silver chloride, and filtered. The hydroxyammonium chloride was titrated with iodine solution. The quantities obtained in separate experiments were thus found to be:—

29.8, 29.1, 32.1, 29.8, 28.9, 30.4 37.4, and 31.6 per cent.

These results show considerable uniformity, with some exceptions, and represent very nearly two-thirds of the hydroxyammonium chloride equivalent to the whole of the nitrogen, that is, 46.33 per cent., two-thirds of which is 30.9. We have no reason to doubt the accuracy of any of these numbers, and attribute the irregularities observable to variations in the proportions of hydrochloric acid taken, although we are not able now to establish this to have been the case in these particular analyses. But, as we shall show that we can make the yield vary to some extent by varying the conditions of the experiment, we do not consider that any special significance is to be attached to the fact that about two-thirds of the nitrogen appears as hydroxyammonium chloride when concentrated acid is used. Uniform procedure has given us uniform results, and by breaking through this we can make the results vary, and can increase the yield of this salt.

For the estimation of formic acid, distillation was necessary before titration could be made, because of the presence of ammonium chlo-

ride. The distillation was finished in a current of air, and the heat so managed as to leave the hydroxyammonium chloride as far as practicable undecomposed.* The formic acid was measured by deducting the quantity of alkali equivalent to the hydrochloric acid found by titration with silver nitrate from the alkali required by the total acid, and calculating the difference as formic acid. In the experiment which gave us the fifth of the enumerated quantities of hydroxyammonium chloride, that is, 28.9 per cent., we obtained 19.8 per cent. of formic acid. The full quantity of formic acid is 30.67 per cent., and two-thirds of this is 20.44, so that we obtained almost two-thirds of the total formic acid possible, just as we obtained nearly two-thirds of the hydroxyammonium chloride.

We have attempted to estimate the formic acid† by weighing the

* We have fewer determinations of formic acid than of hydroxyammonium chloride, because of several failures in measuring it. Some of these were due apparently to the passing over of spray into the receiver in consequence of distilling in small retorts too full, to which practice we were tempted by the difficulty, when the retort was large, of getting over all the formic acid without overheating the hydroxyammonium chloride. This source of error was afterwards avoided by the obvious expedient of distilling with the retort not so full. Other failures were experienced through the presence of a very large excess of hydrochloric acid along with the formic acid, such an excess having been taken in order to keep down by its mass the temperature of the reaction as much as possible, and lessen the production of hydrogen cyanide. Sodium phosphate added to the contents of the retort, to fix some of the hydrochloric acid, rendered the distillation difficult and unsatisfactory. Afterwards, by taking a much smaller proportion of hydrochloric acid, this cause of failure was removed. After all, sufficient determinations for the purpose are given. It is, besides, difficult to see in what way silver fulminate could be decomposed in which the formic acid would not be equivalent to the hydroxyammonium chloride, unless the liberation of much hydrogen cyanide took place.

† In our paper on mercury fulminate we described an experiment in which, by titration of the formic acid from 2.6665 grams of mercury fulminate, and working on thirds, we determined its amount to be 3 per cent. less than the calculated quantity—31.3 instead of 32.4—surely a result having no great pretension to close accuracy, considering that our mercury and hydroxyammonium chloride determinations were in almost perfect accordance with theory. As mercury fulminate has been known since the beginning of this century, as it is 60 years since it was examined by Liebig, and as no analysis of this salt had been published in all that time, except the partial one by Liebig, in which he got 56.9 per cent. mercury instead of 70.4, we thought it of interest to use our results for the purpose of showing for the first time the composition of mercury fulminate by analysis. This having been done by us, Dr. Schotten, in abstracting our paper for the *Berichte der deutsch. chem. Ges.*, has endeavoured to raise doubts in the minds of his readers as to the accuracy of our results. There was and is no better method of determination open to us, a finding by titration of only 97 per cent. of the calculated amount of formic acid was certainly no refinement of accuracy beyond the capability of the method; and a deviation of even double that extent from the truth would still have left our result sufficient to prove all we attempted to make it do. In the text of this paper, we give

calomel produced by it from mercuric chloride, but not with success. H. Rose has proved that in the presence of alkali chlorides, the precipitation of mercurous chloride is incomplete, but this fact was no obstacle to us. We had before us a mixture of formic and hydrochloric acids, and this we proceeded to neutralise with washed precipitated mercuric oxide. To test the method, we operated on lead formate and found it work quite successfully. The lead salt was treated with enough hydrochloric acid to decompose it, and mercuric oxide was then added in excess. Digestion on a water-bath, aided by frequent stirring, and then a second digestion with dilute hydrochloric acid, gave the theoretical quantity of mercurous chloride. In one experiment we got 30·80, in another 30·83 per cent. of formic acid, whilst pure lead formate should yield 30·97 per cent. The method has the great recommendation of depending on the weighing a compound more than ten times heavier than the substance estimated. But unfortunately, as we have said, we found that it would not serve our purpose. The large proportion of hydrochloric acid present proved a fatal obstacle. This acid formed an oxychloride during the long digestion necessary to insure the decomposition of all the formic acid, which it was generally impossible to dissolve out thoroughly from the mercurous chloride by fresh hydrochloric acid, without at the same time decomposing some of it into metal and mercuric chloride. After many trials we gave up our attempt to use this method.

Whatever may be the yellow or orange matter which is formed when the silver fulminate is allowed to grow hot by its reaction with hydrochloric acid, the following experiments serve to show that it is formed at the expense of that portion of the fulminate which would otherwise become hydroxylamine and formic acid in contact with concentrated hydrochloric acid. That it is not formed from the other third of the fulminate, or at least from that third alone, is also to be seen in the fact that, with cooling, only a trace of it is produced, although no portion of this third is gained as formic acid and hydroxyammonium chloride.

In two separate portions, in order to moderate the rise in temperature, 2·6330 grams were drenched with fuming hydrochloric acid, without cooling. The resulting solution, which had a distinct yellow colour, gave, by direct titration with iodine, hydroxyammonium chloride 27·65 per cent., and by titration with alkali, after distillation,

other determinations of formic acid by this method, the degree of accuracy of which may safely be measured approximately by the hydroxyammonium determinations, and as we have suppressed nothing, we offer these to show what the method is capable of. We should add that in all probability the hydroxyammonium is not an exact measure of the formic acid, but measures this and the very small quantity of hydrogen cyanide together.

formic acid 18·67 per cent. These quantities are about one-twelfth less than two-thirds of the whole.

Next, in order to lead to a still greater rise in temperature, 1·9830 grams were treated in one lot in the same way. Much heat was developed, and at first the silver chloride was very strongly coloured, but soon gave up its colouring matter to the solution. The hydroxyammonium chloride was in this case found to be only 21·55 per cent., or less than half the full quantity.

The change in the results obtained by using dilute hydrochloric acid instead of the concentrated, is considerable, and is important as serving to tone down the contrast between mercury fulminate and silver fulminate. Although the use of the acid in the dilute state seems to favour the production of hydrogen cyanide, both hydroxyammonium chloride and formic acid are increased in quantity much above two-thirds. A small quantity of silver fulminate, 0·3175 gram, being put under water, concentrated hydrochloric acid solution was added to the extent of about half the volume. The hydroxyammonium chloride obtained in this case was 43·52 per cent., which is not very far short of the full quantity, 46·33 per cent., whilst the yield with undiluted acid was only 30 per cent., as already fully recorded.

A modification of the preceding experiment was made by using hot liquids. 0·36975 gram of fulminate was placed in hot water, and hot diluted hydrochloric acid added. In this case, 41·60 per cent. of hydroxyammonium chloride was produced, a lower yield, and illustrating the injurious effect of heat.

Once more, 4·28225 grams of fulminate, in two quantities, were treated with cold water and hydrochloric acid, and the resulting solution, after the usual heating on the water-bath, divided into portions in which both hydroxyammonium chloride and formic acid were determined. We found :—

	Per cent.
Hydroxyammonium chloride, by direct titration	42·15
" " weighed as residue on	
evaporation	42·17
Hydroxyammonium chloride, by titration of residue	
with iodine	41·88
Formic acid, by titration with alkali	28·35

From these results, it appears that about nine-tenths of the silver fulminate had become formic acid and hydroxyammonium chloride.

When silver fulminate has been treated with concentrated hydrochloric acid, we always find ammonium chloride present in quantity among the products. In this respect, silver fulminate is in marked contrast with the mercury salts. But when dilute acid is used, this

difference between the salts is no longer observable. Along with the increasing yield of hydroxyammonium chloride and formic acid that attends dilution of the hydrochloric acid, there goes a lessening of the quantity of ammonium chloride down even to nothing.

The results last given show that in the experiment with dilute acid, no ammonium chloride was formed, or practically none, for the difference 0·3 between 42·17 and 41·88 may safely be set down to the presence of water and hydrochloric acid as impurities. Qualitative testing gave only doubtful evidence of any ammonia being present.

In contrast with the result in which dilute hydrochloric acid was employed, may be presented results which were obtained with concentrated hydrochloric acid:—

	I.	II.	III.	IV.
Hydroxyammonium chloride, by direct titration.....	29·80	29·08	32·13	30·42
Mixed chlorides as residue on evaporation	34·90	35·03	37·39	35·37
Hydroxyammonium chloride, by titration of residue	27·60	—	30·07	—
Ammonium chloride, by difference	7·3	—	7·3	—

Although among these experiments II and IV were not followed out, the two numbers given enable the others to be inferred. Ammonia was tested for qualitatively, after destruction of the hydroxyammonium chloride with iodine, and found abundantly. Ammonium chloride 7·3 per cent. is equivalent to more than a fifth of the total nitrogen of the fulminate.

Ammonia, so far, having been determined only by difference in weight between the evaporation-residue and the hydroxyammonium chloride measured by titration, an attempt was made to estimate it directly. Some silver fulminate having been treated with concentrated acid in the usual way, a portion of the solution was treated with copper sulphate and potassium hydroxide in a closed flask, in order to destroy hydroxylamine. The resulting alkaline solution and precipitate were then distilled for ammonia. But the process proved unsatisfactory, inasmuch as free ebullition was impracticable in consequence of the mixture bumping; and therefore only part of the liquid could safely be distilled over, so that some ammonia must have been retained by the copper hydroxide. We succeeded, however, in getting in this way three-fourths of the quantity of the ammonia indicated by the indirect method.

Instead of making further trials to determine the ammonia directly, we made two chlorine determinations in the evaporated residue of chlorides, as well as hydroxyammonium chloride determi-

nations by iodine titration. We found in one case, as difference between total residue and hydroxyammonium chloride, ammonium chloride 4·92 per cent. of the fulminate, and, as the equivalent of the difference between the total chlorine found and that calculated from the hydroxyammonium chloride, 4·33 per cent. ammonium chloride. In the other case we found, as difference by weight, 7·65, and as difference by the chlorine method, 7·20 per cent. ammonium chloride.

These determinations of the chlorine served not only to estimate the ammonia, but also to confirm the view that the oxidisable part of the residue was hydroxyammonium chloride and nothing else.

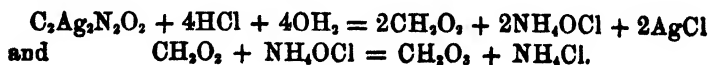
It was in the experiments just detailed that we also determined the hydrogen cyanide, and as the only nitrogenous products we have observed have been hydroxylamine, ammonia, and hydrogen cyanide, the quantities obtained of these three substances should contain all the nitrogen. This they do not quite do, as the following statement shows:—

	I.	II.
Nitrogen as hydroxyammonium....	7·54	6·36
„ ammonia	1·13	1·88
„ hydrogen cyanide	0·15	0·20
„ unaccounted for	0·51	0·89
	<hr/>	<hr/>
„ silver fulminate	9·33	9·33

It is tolerably certain that some ammonia escapes, if not during the evaporation, at least during the drying of the residue in the dish.

Mercury fulminate, when treated with dilute hydrochloric acid, yields no ammonia. By using one measure of concentrated acid to three measures of water, mercury fulminate can be thoroughly decomposed at the heat of a water-bath. The yield of hydroxyammonium chloride is somewhat diminished, and that of hydrogen cyanide increased. Hydroxyammonium chloride, 43·51 per cent., was thus obtained, the calculated quantity being 48·94 per cent.

There no longer exists, therefore, any difference between the two salts as fulminates, what difference they show being caused by the metallic radicals. The same hydrolysis occurs with both fulminates; but in the case of the silver salt, in consequence probably of the sharp separation of the silver chloride in the solid state, the decomposition generates heat so rapidly that the formic acid and hydroxyammonium chloride change into carbonic acid and ammonium chloride:—



Hydrochloric Acid and Fulminurates.

We have only made a special examination of the behaviour of hydrochloric acid with fulminurates, to see whether these salts were capable of generating hydroxyammonium chloride and formic acid. As already known, fulminurates yield some ammonium chloride when heated with aqueous hydrochloric acid. We have experimented with potassium fulminate and silver fulminate, and have obtained neither hydroxyammonium chloride nor formic acid. Hydrochloric acid does not seem to have much action on fulminurates.

Non-production of Oxalic Acid from Fulminates.

We have already published an account of our failure to find even a trace of oxalic acid among the products of decomposition of mercury fulminate by sulphuric acid, or by aqueous hydrogen sulphide. But as it is stated that Steiner got oxalic acid by decomposing mercury fulminate with hydrogen sulphide, using ether instead of water as a menstruum, and even to have obtained it in crystals (see *Watts's Dictionary*), we have followed his process, using as little ether as practicable, so as to avoid as far as possible the accidental presence of water. We have repeated the experiment, and on evaporating the ethereal solution, after saturating it with hydrogen sulphide, as directed, could find no trace of oxalic acid in the residue, and for our own part we believe that oxalic acid cannot be produced from fulminates by any method yet published.

VIII.—*On the Constitution of Fulminates.*

By EDWARD DIVERS, M.D.

Since I laid before the Society my conclusion as to the probable constitution of the fulminates being different from any previously attributed to it, Kawakita and myself have shown the improbability of Liebig having really obtained silver fulminate without the co-operation of nitric acid with the nitrous acid, and are glad to have had the correctness of our results upheld by Armstrong on theoretical grounds. In accepting also my criticism of his own formula for the fulminates, Armstrong pointed out at the same time that in representing the formation of the silver fulminate from alcohol and nitrous acid, as I did, I had laid myself open to like criticism. This is true, and it is a relief to me to know that this change which my formula

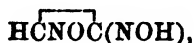
for fulminates could not legitimately represent can no longer be regarded as possible.

I was led by this formula to doubt whether Kekulé's dibromonitro-acetonitrile could have the constitution expressed by its name, and pointed out that it should probably be represented by the formula $O:C:N.O.N:C:Br_2$. I have not yet fulfilled my intention of examining this body, but have seen the original communication in the *Berichte*, 5, 89, by Sell and Biedermann, describing the corresponding iodine compound, and see by it how little further examination is really necessary to show that the carbons of these bodies are not directly joined. These chemists have found that the end-product of hydrogenising the iodine compound by tin and hydrochloric acid is methylamine, and that the formation of this body is preceded by that of abundance of hydrogen cyanide. This appears to me conclusive evidence that the carbons are not directly united. Hydrolysis seems highly improbable as a cause of the separation of the carbon-atoms, supposed to be united, because these haloid compounds have already been produced by the action of bromine or iodine in presence of water.

Armstrong has amended his original formula. He suggests a theory of the conversion of alcohol into fulminate, in which the alcohol first becomes hydroxyethylaldehydrol, and is then acted on half by hydroxylamine and half by nitrous acid. To the latter part of this theory I cannot assent, as I do not believe that these bodies can act without mutual destruction or destruction of each other's derivatives.

As regards the formula he now proposes for the fulminates, it is unfortunate that this is given in an erroneous form in his note. A correction of it has since been made in the list of the *errata*, which I will venture to suggest still requires amending. According to the

correction, fulminic acid is $HOC\overline{NC}(NOH)$, and this allows of no explanation of the conversion of both nitrogens into hydroxylamine, and must therefore, in my opinion, be rejected. I had previously corrected his formula for myself, as originally given, to



and find that Schotten has done the same for the *Referate* of the *Berichte*. Even when I assume that this formula really represents Armstrong's present views, I can hardly agree with him in regarding it as differing but slightly from that which he brought forward in 1875, namely, $(NO)HC:C(NO)$. For not to insist on the importance of the difference between an ethylene and an ethane type, I see a profound difference between them, in that one of the atoms of

oxygen unites carbon to nitrogen in the present formula, whilst it is only united to nitrogen in the earlier one.

In many respect the formula $\overline{\text{HCNOC}}(\text{NOH})$ is as satisfactory as the one proposed by me, $\overline{\text{HCNONCOH}}$. But I find a strong argument in favour of the latter in the fact that it shows the hydroxyl in union with nitrogenised carbon, and naturally, therefore, as in cyanic acid, markedly basic. In the other formula, the hydroxyl of a hydroxylamine derivative is represented not only as basic, but as capable even of taking part without difficulty in double decompositions in water, and yielding the various bimetallic fulminates. But so far as I know, the hydroxyl of hydroxylamine has proved itself to be analogous to "alcoholic" hydroxyl in carbon compounds, its hydrogen being replaceable by organic radicals only, and not by metals in presence of water, if at all. Schramm's hydroxylamine compounds, containing silver or sodium, may or may not be metaloxyl-derivatives. The sodium compound appears unable to exist in water. I have only to add that I see my use of the radical :N.O.N: has the support of Goldschmidt, who, a little before my paper on the fulminates was published, had used it in representing the possible constitution of a dioximido-derivative of phenanthraquinone.

Note on the above by Dr. Armstrong.

My chief object in publishing a "note on the formation and constitution of the fulminates" was to call attention to what I believe to be the fact, viz., that the fulminate is not the immediate product of the action of nitrous acid on alcohol in presence of mercury or silver salt; and to indicate a direction in which, in my opinion, synthetical experiments should be prosecuted. With reference to Dr. Divers' criticism, although nitrous acid and hydroxylamine tend to destroy each other, yet I believe it to be both possible and probable that they may be generated side by side without mutual destruction, if a third body is present with which one or both may enter into reaction, or which tends to exercise a protective influence. His own remarkable observations on the action of tin on a mixture of nitric and chlorhydric acids may be cited in support of this view.

My formula was not put forward as a final expression of the properties of the fulminates; as I particularly stated, the formula printed—or rather which should have been printed, N.C.OH
 $\text{N.C(N.OH)'}^{\text{'}}$ was not the only one which could be deduced. The two formulæ

which I incline to regard as the most probable are, however, the following:—



But while I am of opinion that these formulæ fully take into account both the elimination of the two nitrogen-atoms as hydroxylamine and also the formation of bimetallic fulminates, I do not think we can at present further discuss with advantage the several formulæ put forward by Divers and myself; they, however, will doubtless serve to guide us both in investigating the subject, and in obtaining evidence which may ultimately furnish a solution of the problem.

I may here point out that although the fulminates have hitherto always been regarded as "dicarbon" derivatives, on account of their formation from ethyl alcohol, there is no direct evidence before us that such is actually the case, and it is especially noteworthy that Divers has always failed to obtain oxalic acid by hydrolysis of fulminates.

IX.—Notes on the Chemical Alterations in Green Fodder during its Conversion into Ensilage.

By CLIFFORD RICHARDSON, Assistant Chemist U.S. Department of Agriculture.

In recent numbers of the *Journal of the Chemical Society*, Professor Edward Kinch and Dr. O. Kellner have published some observations on the changes which take place in the nitrogenous constituents of fodders.

Analyses which I have made during the past two years throw additional light on the subject, and are, although somewhat incomplete, presented here.

Professor Kinch found that 55 per cent. of the total nitrogen present in the ensilage of grass was of a non-albuminoid nature, whilst in the original grass only 9 per cent. was of this form. In the case of mangel leaves Kellner found that of the total nitrogen present 27.8 per cent. in the original leaves, 45.5 per cent. in the ensilage, and as much as 59.7 per cent. in the ensilage preserved in stoppered jars was non-albuminoid. In the ensilage of maize I have found:—

	Per cent. of total nitrogen as non-albuminoid.
Original stalks.....	21·2
Ensilage No. 1.....	44·6
Ensilage No. 2.....	49·6
Dried fodder	15·6
Ensilage from young maize	53·3
Ensilage from older maize.....	47·1

These results with grass, mangels, and maize show that in the conditions existing in silos a large portion of the albuminoids are converted into non-albuminoid nitrogenous substances, whilst in the ordinary drying of fodder no such change seems to take place.

Kinch and Kellner both found that a portion of the nitrogen of the original plant was lost or did not appear in the analysis. With grass it was 13 per cent.; with mangels 27·8 per cent. in the unpressed ensilage in the jar, and as much as 59·8 per cent. in that in the open silo. The latter high percentage is doubtless due to the carrying away in the expressed juice of much soluble nitrogenous substance. I am in possession of but few quantitative data in regard to maize, but have found that in the samples of ensilage which I have examined there is a comparatively large amount of ammonia combined with the acids produced by fermentation, acetic and lactic, which of course is lost in drying the specimens for analysis. In the results, this produces an apparent loss of nitrogen in the ensilage itself: it is at any rate a loss of nitrogen of nutritive value. A quantitative determination of the ammonia salts in one specimen of ensilage (Serial No. 1693) gave the following results:—

Weight of ensilage taken	4000·0
Equivalent to dry substance	620·0
Weight of NH_4Cl	8·660
Equivalent to nitrogen.....	2·266
Per cent. of nitrogen from dry substance	0·366
Equivalent to albuminoids	2·287

That the nitrogen was in the form of ammonia and not a more complex amine was proved by the following analysis:—

Weight of ammonia salt taken	0·1000
Weight of platinochloride found	0·4105
Equivalent to NH_4Cl	0·0990

This ammonia salt, probably acetate, would be lost in the process of drying, and produce a corresponding deficit in the relative percentage of nitrogen in the analysis. In fact, a loss of 2·29 per cent. of albuminoids in the dry substance of an average maize stalk, con-

taining 7.50 per cent., amounts to a little more than 30 per cent. of the total nitrogenous substance in the plant, and to about the loss which Kellner found in his experiments with mangel leaves not under pressure. The remaining non-albuminoid nitrogen is probably largely of an amide nature, as, like Kellner, I have found very small amounts of peptones. Attempts, however, to separate any amides in a crystalline condition have resulted in obtaining nothing but a syrupy nitrogenous substance.

The loss of nitrogenous substance from conversion into ammonium salts and decomposition on drying is relatively compensated for by the large loss of carbohydrates, so that in the analytical figures neither loss is prominent, and they are at first glance deceptive. The control of course lies in an absolute knowledge of the weight lost by the fodder in the silo, or in the relative increase in one of the constituents which is less liable to change, as for instance the ash. But as Kellner has shown, pressure is very liable to remove the soluble part of the ash in the juice expressed, and thus entire dependence cannot be placed on this element.

An interesting experiment was carried on at the New Jersey Experiment Station in 1881, in which the ash served as a basis for calculation without apparently vitiating the results.

Ten tons of green fodder "corn" was divided into two lots on September 1st, one half being stacked in the field, and the other packed in a silo of the capacity of 12 tons, after being cut in short lengths. At the same time, a carefully selected sample of the green fodder was prepared for analysis. In November, 1200 lbs. of the dried fodder was run through a cutter, and an average sample prepared for analysis. On the 23rd of December a specimen of the ensilage was selected. The composition of the three substances was as follows:—

Original substance—	Green stalks.	Dried stalks.	Ensilage.
Water	75.00	39.37	74.50
Ash	1.58	4.63	1.97
Fat.....	0.22	0.66	0.27
N.-free extract....	15.60	32.85	13.58
Crude fibre	6.35	18.65	7.92
Crude albumin....	1.25	3.84	1.76
	100.00	100.00	100.00

Dry substance—

Ash	6.32	7.64	7.71
Fat	0.88	1.09	1.06
N.-free extract....	62.40	54.18	53.24
Crude fibre	25.40	30.76	31.07
Crude albumin....	5.00	6.33	6.92
	100.00	100.00	100.00

As 100 lbs. of the dry matter of the green fodder contained 6.32 lbs. of ash, the amounts of the other constituents corresponding with this weight of ash and therefore with each original 100 lbs. of stalks, were calculated in order to show the absolute loss of each constituent.

	Green stalks.	Dried stalks.	Ensilage.
Ash	6.32	6.32	6.32
Fat	0.88	0.90	0.86
N.-free extract	62.40	44.82	43.64
Crude fibre.....	25.40	25.44	25.49
Crude albumin	5.00	5.24	5.67
Total weight of dry matter to 6.32 lbs. of ash	100.00	82.72	81.98

The loss in this case is seen to fall upon the carbohydrates entirely, and to be as great for the dry fodder as for the ensilage. There is an apparent slight increase in albuminoids, which can be explained by the fact that the calculation is made as if no ash had been lost by being dissolved or expressed in the two preserved samples. This is remarkable as showing that in this case, quite at variance with other instances, the nitrogen suffered little or no loss, and that in fact the whole loss fell upon the carbohydrates. This may be due to the short time during which the maize was in the silo, as all samples which I have examined have not been taken out for several months.

These results at least show how varied the conditions are and how unsafe it is to generalise from any one experiment. This point is made evident in the analyses appended to this paper.

As to the nature of the fermentation and the proximate principles involved, I have made some observations. In but one sample out of many examined has any trace of *Saccharomyces* been found. As a rule the juice expressed from the fresh ensilage is swarming with *Bacillus subtilis*, together with some species of *Bacterium* and *Micrococcus*. No signs of the ordinary lactic or viscous ferment have been observed. The fermentation does not appear therefore to be of an alcoholic nature, or similar to any with which we are well acquainted. Analyses show the presence of an insufficient amount of alcohol, gum,

or free acid for any of the usual forms of fermentation, as can be seen from the following determinations.

Alcohol was never absent in any of the ensilages experimented on, but in all was present in such small quantities as to be distinguished only by the iodoform test.

Lactic acid has always been detected, but never in large quantity. Acetic acid is the chief acid of the ensilage. The relative proportion of the two acids varies largely, the following being a few determinations:—

Serial No.	Per cent. in ensilage of	
	Lactic acid.	Acetic acid.
1003	traces	2.12
1004	0.15	1.59
1500	0.52	0.80
1501	0.24	undet.
1502	0.26	1.02
1677	0.13	undet.
1693	0.11	undet.
		Total as acetic acid.
1840		2.40
1841		1.42

The whole amount of acid present was from 1 to over 2 per cent., the lactic acid not rising above six-tenths of a per cent.

The presence of lactic acid was determined by expressing the juice from a specimen of ensilage, distilling off the volatile acetic acid by repeated distillations, and neutralising the residue with zinc carbonate. The crystals of zinc lactate which were obtained on evaporation were crystallised and analysed. They contained:—

	Analysis.	Theory.
Water	18.46	18.18
ZnO	26.71	27.27

Gum or similar substance is not formed in any large amounts in the silo.

Unchanged sugar has been found in the juice expressed from two ensilages, but as a rule it completely disappears. No. 1003 contained 2.40 per cent., No. 1004 1.07, and No. 1541 0.76 per cent. of reducing sugars.

The fibre is of course increased in relative amount, but absolutely it is probable that it is but slightly altered.

In Table I (pp. 85-86) analyses of a number of ensilages are presented together with those of a dried fodder and several green stalks at

TABLE I.—Analyses of Maize Silage and of Maize Fodder.

	Silage. *1903.	Silage. 1904.	Silage. 1906. Frsh.	Silage. 1901. Oat 24 hours.	Silage. 1902. (Newbit.)	Silage. 1940.	Silage. 1941.
Original substance—							
Water.....	77.30	74.10	81.20	81.40	84.00	70.60	84.80
Ash.....	2.01	1.44	1.36	1.44	1.25	2.00	0.91
Oil, &c.....	1.90	1.74	1.71	1.21	1.20	1.80	1.00
Nitrogen-free extract.....	11.24	12.87	9.14	9.47	7.75	15.37	9.40
Crude fibre.....	5.71	7.04	4.88	4.84	3.88	7.54	2.85
N x 6.25 = "albuminoids".....	1.04	2.77	1.71	1.64	1.92	2.69	1.04
	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Dry substance—							
Ash.....	8.87	5.72	7.21	7.76	7.83	6.81	5.98
Oil, &c.....	7.91	6.73	9.12	6.49	7.53	6.12	6.60
Nitrogen-free extract.....	49.50	49.69	48.59	50.90	48.43	62.26	61.84
Crude fibre.....	25.15	27.19	25.98	26.05	24.24	25.65	18.76
N x 6.25 = "albuminoids".....	8.57	10.67	9.10	8.80	11.97	9.16	6.82
	100.00	100.00	100.00	100.00	100.00	100.00	100.00
In the ether extract—							
Non-volatile free acid.....	trace	0.56	2.99	1.28	1.65	—	—
In the nitrogen-free extract—							
Sugar, &c., sol. in 60 per cent. alcohol.....	17.76	15.54	—	—	—	—	—
Substances, sol. in 80 per cent. alcohol; insol. in water.....	3.86	3.14	—	—	—	—	—
Gum, &c.....	2.10	2.89	—	—	—	—	—
In the "albuminoids" —							
Nitrogen.....	1.37	1.71	1.45	1.40	1.91	1.47	1.09
Non-albuminoid nitrogen.....	—	—	—	—	—	—	—
Per cent. of nitrogen as non-albuminoid.....	—	—	—	—	—	—	—
In the original substance—							
Acetic acid.....	2.12	1.59	0.80	—	1.02	2.40	1.22
Lactic acid.....	trace	0.15	0.52	0.24	0.26	—	—
Juice per cent.....	47.5	40.5	39.5	29.1	49.3	50.8	—
Sp. gr.....	1.046	1.0335	1.0197	1.0910	1.017	—	—
Sugars.....	2.40	1.07	None	None	None	—	0.76
Acids.....	—	8.14	4.67	4.27	4.03	—	—

* 1902, 1942, 1941 from Virginia; 1904, 1952, 1953 from New York State; 1900, 1901, 1907, 1917, 1933 from Indiana.

TABLE I continued.—Analyses of Maize Silage and of Maize Fodder.

	Silage. 1677. (Blair.)	Silage. 1693. (Blair.)	Silage. 1692. (Young.)	Silage. 1693. (Old.)	Dried fodder. 1694.	Green fodder. 1624. St lks for 1677 and 1693.	Stalks. Egyptian maize. Young anthers just out.
Original substance—							
Water.....	81.67	84.50	82.64	78.62	27.25	85.96	84.90
Ash.....	1.04	1.04	1.14	1.21	2.12	1.87	1.11
Oil, &c.....	1.09	0.79	1.01	1.46	2.53	0.82	0.44
Nitrogen-free extract.....	10.17	8.47	9.21	11.39	60.02	7.27	9.25
Crude fibre.....	4.64	3.86	4.96	5.80	12.75	2.48	3.04
N x 6.25 = "albuminoids".....	1.39	1.34	1.04	1.52	5.33	1.90	1.28
100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Dry substance—							
Ash.....	5.68	6.68	6.69	5.68	2.91	13.31	7.39
Oil, &c.....	5.96	5.08	5.84	6.82	3.18	3.71	2.89
Nitrogen-free extract.....	53.50	54.64	53.02	53.26	68.76	61.77	61.25
Crude fibre.....	25.30	24.93	28.58	27.12	17.42	17.67	20.15
N x 6.25 = "albuminoids".....	7.86	8.67	5.97	7.12	7.33	13.54	8.82
100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
In the ether extract—							
Non-volatile free acid.....	0.72	0.72	—	—	—	—	—
In the nitrogen-free extract—							
Sugar, &c., sol. in 80 per cent. alcohol; sol. in water.....	10.59	8.34	—	—	—	10.02	20.32
Substances, sol. in 80 per cent. alcohol; insol. in water.....	2.90	3.66	—	—	—	2.64	7.17
Gum, &c.....	2.91	3.58	—	—	—	2.64	2.29
In the "albuminoids"—							
Nitrogen.....	1.21	1.39	0.95	1.14	1.18	2.17	1.88
Non-albuminoid nitrogen.....	0.54	0.69	0.51	0.54	0.19	0.46	—
Per cent. of nitrogen as non-albuminoid.....	44.6	49.6	53.3	57.1	16.6	2.02	—
In the original substance—							
Acetic acid.....	—	—	—	—	—	—	—
Lactic acid.....	—	—	—	—	—	—	—
Juice per cent.....	0.13	0.11	—	—	—	—	—
Sugars.....	—	—	—	—	—	—	—
Solids.....	—	—	—	—	—	—	—

various stages of development. From them, much may be learned as to the variations to be expected.

The composition of the stalks of green maize is subject to very wide variations, as may be seen by the few analyses quoted. This then is a primary cause of differences in the composition of the ensilage, and, although it is due largely to the period of growth at which the stalks are cut, yet there are often marked differences in composition in those of the same stage of development, even in the same field.

In a series of analyses of the stalks of Egyptian sugar corn and Lindsay's horse-tooth corn, completed by me, and published in the Report of the Commissioner of Agriculture for 1881 and 1882, these variations are shown. The specimens, the analysis of which are here given, were all from a small plot of carefully selected stalks only a few rods square, and yet, in many instances, they show the largest variations from a regular series.

The variations which are found in the composition of the stalks while they are in a condition to be packed in a silo, that is to say, from the appearing of the tops until the grain is well formed, are included within the following limits:—

	Highest.	Lowest.
Water in green substance	91.60	79.10
Dry substance.....	20.90	8.40
Ash	9.72	3.54
Oil	3.48	1.68
Carbohydrates.....	69.40	59.60
Crude fibre.....	31.29	21.56
Albuminoids	11.53	1.67
Percentage of nitrogen as non-albuminoid	70.4	18.0

These limits, together with a study of the individual analyses, serve to show the primary cause of the differences in ensilages.

As to variations produced by other causes, illustrations are found in the samples numbered 1652, 1653, 1677, and 1693.

Numbers 1652 and 1653 are analyses of ensilage from young and old stalks. The younger would naturally contain more ash and albuminoids as it went into the silo, but the nitrogenous substances would be in such a condition, from the greater amount of soluble nitrogen, as to make them more liable to conversion into ammonium salts. This is the case with No. 1652. In it, the ash is higher than in the older specimen, but the nitrogen is lower from a greater loss. The relative amount of non-albuminoid nitrogen is also lower in the younger than in the older sample. In other respects, they do not differ largely, although one was from stalks on which the ears were well formed, and

TABLE II.—*Egyptian Sugar Corn (Maize), planted April 30th, 1881.*

	Stalks.						
	526. July 5th, top just out.	540. July 11th, anthers not out.	547. July 11th, anthers out, filling.	562. July 18th.	576. July 25th, silk out.	580. August 1st, ear formed.	694. August 8th.
Development—							
Height, in feet	7.0	7.2	8.5	9.0	9.2	10.2	10.0
Diameter, in inches	1.2	1.2	1.1	1.2	1.2	1.6	1.2
Total weight, in grams	1242.0	1097.0	1037.0	1378.0	1642.0	1722.0	1068.0
Weight of stalk	980.0	585.0	5.42	615.0	575.0	636.0	593.0
" leaves	216.0	468.0	430.0	651.0	737.0	864.0	300.0
" top	66.0	44.0	35.0	26.0	78.0	32.0	9.0
" ear	—	—	—	83.0	252.0	190.0	166.0
Per cent. of stalk in whole plant	77.3	53.3	52.1	44.9	35.0	37.0	55.5
Dry substance—							
Ash	9.72	9.09	6.53	5.60	4.81	5.87	4.97
Crude fat	2.58	1.80	1.68	3.48	2.75	2.35	2.10
Nitrogen-free extract	50.60	51.20	52.41	60.45	61.53	66.72	67.37
Crude fibre	27.01	26.38	31.29	28.04	26.09	22.07	21.82
Crude albumin	10.09	11.53	8.09	4.43	4.85	2.99	3.74
Total nitrogen	1.61	1.85	1.29	0.71	0.78	0.48	0.60
Non-albuminoid nitrogen	0.99	1.27	0.85	0.31	0.39	0.29	0.33
Per cent. of nitrogen as non-albuminoid	61.4	68.6	65.9	43.7	50.0	60.5	55.0
Original substance—							
Water	91.60	91.30	88.30	85.90	83.20	80.20	80.60
Ash	0.82	0.79	0.76	0.79	0.81	1.16	0.96
Crude fat	0.21	0.16	0.19	0.40	0.46	0.47	0.41
Nitrogen-free extract	4.25	4.15	6.14	8.53	10.34	13.21	13.07
Crude fibre	2.27	2.30	3.66	3.67	4.38	4.37	4.24
Crude albumin	0.85	1.01	0.95	0.62	0.81	0.59	0.73

the other from stalks on which the ears had made no appearance. In comparison with the ensilages, the dried fodder, No. 1654, from stalks of the same field as the old ensilage, No. 1652, shows several advantages. As has been already remarked, its nitrogenous constituents have not suffered so much change, only 15·6 per cent. being in a non-albuminoïd form as compared with 53·3 and 47·1 per cent. in the ensilages. A smaller loss of carbohydrates has left the relative percentages of fibre, fat, and ash, low; and the evidence points to the fact that the stalks must have dried rapidly and with few changes, furnishing a fodder of much better composition than that analysed in New Jersey.

In Nos. 1677 and 1693, we have analyses of two specimens of ensilage taken from the same silo within a few days of each other. One has lost more ash and nitrogen than the other, and this is due probably to greater pressure on the first sample, which had lost expressed juice carrying with it nitrogenous matter and ash. In other respects they are much alike. The variations in composition, which are found among the analyses of ensilage, lie within the following limits:—

	Highest.	Lowest.
Water	84·80	70·60
Ash	2·01	0·91
Oil	1·80	0·79
Carbohydrates	15·37	7·75
Fibre	7·54	2·85
Albuminoïds (N × 6·25) ..	2·77	1·04
Per cent. of nitrogen as non-albuminoïd	53·3	47·1
Or for dry substance—		
Dry substance	15·20	29·40
Ash	8·87	5·68
Oil	9·12	5·08
Carbohydrates	61·84	48·43
Fibre	28·58	18·76
Albuminoïds	11·97	5·97

By comparison with the extremes for green stalks, it is seen that the albuminoïds are higher in the dry substance of one of the ensilages, No. 1502, than in the dry substance of any of the stalks. The high figures in the ensilage are probably only relative, due to a great loss of carbohydrates and little change of albuminoïds.

Exact quantitative experiments are greatly to be desired, in order that we may have some explanation of the interesting changes which undoubtedly occur.

Washington, October, 1884.

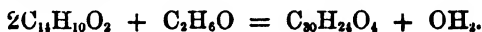
X.—On Condensation Compounds of Benzil with Ethyl Alcohol.

By FRANCIS R. JAPP, M.A., Ph.D., and Miss MARY E. OWENS,
B.S. (Cincinnati).

IN preparing benzoic acid by heating benzil with alcoholic potash, Jena (*Annalen*, 155, 79) observed the formation of a neutral compound, melting at 200° , to which he ascribed the formula $C_{14}H_{12}O_2$, regarding it as isomeric with benzoïn. He assigned to it the name *tolane alcohol*. The quantity at his disposal was insufficient for further investigation.

Limpricht and Schwanert (*Ber.*, 4, 335) obtained the same compound by heating together benzoïn and alcoholic potash with access of air. They arrive at the conclusion that it is a derivative of benzoïn (although they show in the same experiment that benzil is formed under the above conditions by the oxidising action of the air upon the benzoïn), and state their suspicion that the benzil employed by Jena must have contained benzoïn. On the strength of their analyses (not published) they arrive at the formula $C_{30}H_{24}O_4$, and name the compound *ethylidibenzoïn*.

We have found that, by the protracted action of very dilute alcoholic potash on benzil in the cold, the above compound is formed in large quantity. The yield, amounting in one experiment to 6 grams from 10 grams of carefully purified benzil, quite precludes the possibility of a formation from benzoïn present as an impurity. Our analyses lead to the formula $C_{30}H_{24}O_4$, which differs from that of Limpricht and Schwanert by containing two atoms of hydrogen fewer. The formation of such a compound from benzil and alcohol might be expressed by the equation—



In order to prepare this compound, 10 grams of caustic potash were dissolved in $2\frac{1}{2}$ litres of alcohol, and to the solution thus obtained 200 grams of finely powdered benzil were added. The whole was shaken until the liquid was saturated with benzil, after which it was allowed to stand, shaking from time to time. The separation of the compound begins at the end of the first or second day, and is practically complete in about a fortnight. It is thus obtained as a crystalline powder, but, when a larger quantity of alcohol is employed, so as to have all the benzil in solution from the commencement, it separates in moderately large lustrous crystals.

The crude substance was washed with ether, to remove unaltered benzil, and then recrystallised, first from benzene, and afterwards from

alcohol. The latter solvent deposits the compound in small lustrous crystals. These contain alcohol of crystallisation, which they lose only after long heating at 120° . At 100° they are permanent. The compound, thus freed from alcohol, melted at $200-201^{\circ}$, and yielded on analysis numbers agreeing with the formula $C_{30}H_{24}O_4$. We append, for the sake of comparison, the theory for Limpricht and Schwanert's formula $C_{30}H_{26}O_4$:—

	Substance.	CO ₂ .	OH ₂ .
I.	0.1258	0.3694	0.0612
II.	0.1448	0.4260	0.0702

	Calculated for $C_{30}H_{24}O_4$. (Japp and Owens.)	Calculated for $C_{30}H_{26}O_4$. (Limpricht and Schwanert.)	Found.	
			I.	II.
C	80.36	80.00	80.03	80.24
H	5.36	5.78	5.41	5.38
O	14.28	14.22	—	—
	<hr/> 100.00	<hr/> 100.00		

The difference in the percentages required by the two formulæ is certainly rather small for analysis alone to decide between them, but we think that the mode of formation which we have just described renders the first formula the more probable. Further, if the second formula were correct, the errors of analysis, both for carbon and hydrogen, would be in the wrong direction, whereas with the first formula the errors are in the usual direction.

We think that the results obtained by our predecessors are possibly due to their having overlooked the alcohol of crystallisation, or, at all events, to their not having taken into account the difficulty of completely expelling this alcohol. They crystallised the substance from alcohol, but none of them mention the presence of alcohol of crystallisation. Jena appears to have analysed a compound from which only a portion of the alcohol had been expelled. Thus, the formula $C_{30}H_{24}O_4 \cdot C_7H_6O$ requires C 77.73 and H 6.07 per cent., whilst Jena finds C 78.7 and H 5.8 per cent., or values intermediate between the foregoing and those required for the formula $C_{30}H_{24}O_4$. A similar, though smaller, error may have lowered the carbon and raised the hydrogen in Limpricht and Schwanert's analyses. The melting point of the substance analysed would probably afford no intimation of the presence of the alcohol, for we have found that the crystals containing alcohol do not, unless the temperature is rapidly raised in determining the melting point, melt lower than those from which the alcohol has been previously expelled.

A determination of alcohol of crystallisation was made, with the following result:—

1.3890 gram of crystallised substance, on heating at 120° , lost 0.1284 gram.

	Calculated for $C_{30}H_{24}O_4, C_2H_6O$.	Found.
Alcohol in 100 parts. . . .	9.31	9.24

As the percentage of hydrogen in the compound $C_{30}H_{24}O_4, C_2H_6O$ differs from that of a compound of the formula $C_{30}H_{26}O_4, C_2H_6O$, we analysed a specimen of the air-dried substance containing alcohol of crystallisation:—

Substance.	CO ₂ .		OH ₂ .
0.1145	0.3256		0.0619
	Calculated for $C_{30}H_{24}O_4, C_2H_6O$.		Found.
C ₃₂	384	77.73	77.55
H ₃₀	30	6.07	6.01
O ₅	80	16.20	—
	494	100.00	

The formula $C_{30}H_{26}O_4, C_2H_6O$, on the other hand, requires C 77.42 and H 6.45 per cent. The value obtained for hydrogen, coupled with that yielded by the compound dried at 120° , appears to us to afford strong evidence in favour of the formula with less hydrogen.

From a solution in hot benzene, the condensation-product is deposited in minute rhomboidal plates generally grouped in rosettes, and containing benzene of crystallisation. The crystals, when exposed to the air, effloresce and become opaque. A portion of the crystallised substance, freed from adhering benzene by pressure between filter-paper and brief exposure to the air, on heating at 120° , lost 14.96 per cent. of its weight. The formula $C_{30}H_{24}O_4, C_2H_6O$ requires a loss of 14.83 per cent.

Limpricht and Schwanert (*loc. cit.*) state that by heating "ethyldibenzoin" with acetyl chloride, a monacetyl-derivative melting at 145° is obtained. We have been unable to confirm this result. The substance may be heated for an hour with acetyl chloride at 100° without undergoing change. Protracted heating, or a higher temperature, produces resinification. We were equally unable to obtain an acetyl-derivative by boiling the substance with acetic anhydride. We have, however, made an observation which, we think, explains the supposed existence of a monacetyl-derivative. When the condensation-product is recrystallised several times from glacial acetic acid, the melting

point sinks each time, until a limit is reached, when a substance is obtained melting at about 130° . This limit may be reached in a single crystallisation, by boiling the compound for some hours with the acetic acid. The substance thus obtained is not an acetyl-derivative, but a compound of the condensation-product with acetic acid (or possibly with acetyl and hydroxyl). On exposure to the air, and more rapidly on heating, it parts with acetic acid; and its melting point lies anywhere between 130° and 200° (the melting point of the original substance), according to the amount of drying to which it has been subjected. It is possible that Limpricht and Schwanert, if they employed acetic acid as a solvent, may have obtained this molecular compound, and analysed a product from which the acetic acid had been only partially expelled. This would account for the melting point found by these investigators; and the substance in this condition would also give figures agreeing more or less with those required for a monacetyl-derivative, seeing that the composition of such a derivative lies almost intermediate between that of the molecular compound and that of the original condensation-product.

Calculated for			
	$C_{30}H_{24}O_4, C_2H_4O_2$	$C_{30}H_{23}(C_2H_3O)O_4$	$C_{30}H_{24}O_4$
C	75.59	78.37	80.36
H	5.51	5.31	5.36
O	18.90	16.32	14.28
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

A specimen of the molecular compound, melting at 133° , gave on analysis C 75.48 and H 5.34 per cent.

As Limpricht and Schwanert publish no details of preparation, or analytical figures, in connection with their acetyl compound, we have no means of testing the correctness of the above supposition.

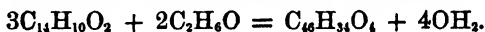
In the benzene mother-liquors remaining from the purification of the foregoing condensation-product, we found a second substance, which was deposited in minute yellow crystals melting at 232° . A larger quantity of this substance was obtained from the original alcoholic potash mother-liquors (after removing the compound $C_{30}H_{24}O_4$), by acidifying with hydrochloric acid, distilling off the alcohol to a small bulk, and precipitating the organic substance by the addition of water. This precipitated substance was treated with alcohol, in order to remove benzoic acid and a soluble resin, and the crystalline residue was dissolved in hot phenol, and reprecipitated with alcohol. By a repetition of this crystallisation from phenol, the substance was

obtained as a yellow crystalline powder, melting as above at 232° . Analysis gave numbers agreeing with the formula $C_{46}H_{34}O_4$:—

	Substance.		CO ₂ .	OH ₂ .	
I	0.1354		0.4204	0.0657	
II	0.1534		0.4769	0.0742	
III	0.1492		0.4640	0.0735	
	Calculated for		Found.		
	$C_{46}H_{34}O_4$.		I.	III.	III.
C ₄₆	552	84.92	84.67	84.78	84.81
H ₃₄ ..	34	5.23	5.39	5.37	5.47
O ₄	64	9.85	—	—	—
	650	100.00			

These analyses were made with different preparations.

The formation of a compound of the above formula from benzil and alcohol may be expressed by the following equation :—



We have also found that dilute alcoholic potash acts slowly on benzoïn in the cold, and, when air is excluded during the reaction, gradually converts it into a compound crystallising in silky needles, which melt at 250° , and are apparently distinct from any of the compounds hitherto obtained by the action of potash on benzoïn. An account of this reaction is reserved for a future communication.

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South Kensington.*

XI.—*Note on the Solubility of Certain Salts in Fused Sodium Nitrate.*

By F. BICKELL GUTHRIE, Demonstrator of Chemistry, Queen's College, Cork.

At the suggestion of my father, I have examined the solubility of certain salts in fused sodium nitrate.

The salts examined are the barium, strontium, calcium, and lead sulphates, chromates, and carbonates. All of these may be classed as salts sparingly soluble in water, some of them as characteristically so, and all of them are certainly less soluble at ordinary temperatures in neutral media, such as alcohol or benzene, than in water itself.

It is well known that solution occurs also when such salts are brought into contact with aqueous solutions of other salts.

The present communication is a contribution to the study of anhydrous solubility, which has the same right to be considered a dissolution as distinguished from chemical decomposition, as has the dissolution of nitre in water. Whether or no double decomposition may be supposed to occur is beyond the scope of the present inquiry.

I find that when one of the above salts is heated with fused sodium nitrate, a certain proportion of it enters into fusion, that this proportion is greater the higher the temperature, and that the excess is redelivered as an unaltered solid when the liquid cools. Under the proper limitation of definition, then, I take it that we have as clear a case of dissolution, as when sugar dissolves in water.

The sodium nitrate obtained from the manufacturer as "pure recrystallised," was again purified by crystallisation, and then fused in a porcelain crucible. The dry and pure salts were added to it in small portions at a time, and well stirred, until a fresh quantity remained undissolved. The mass was then allowed to cool quietly, so that not only the excess of the added salt, but also a considerable amount of the eutectic alloy, had solidified. The liquid body was then poured on to a cold slab and analysed.

No attempt was made to determine the temperature of fusion or solidification of such alloys. Their temperatures of fusion are so nearly identical in every case with that of the nitrate that such attempt at discrimination would be misleading. The added salts were prepared by precipitation in the usual manner, and carefully dried. The following are the results of analyses :—

Barium Carbonate and Sodium Nitrate.

- (1.) 8.1347 grams treated with hot water and a little ammonia gave 0.0763 gram on ignition, or 0.936 per cent.
 - (2.) 6.8604 grams gave 0.0615 gram, or 0.896 per cent.
- Mean = 0.916 per cent.

Strontium Carbonate.

- (1.) 6.0918 grams treated with hot water and a little ammonia, on filtration and gentle ignition, gave 0.0541 gram, or 0.88 per cent.
- (2.) 8.6506 grams treated in the same way gave 0.0431 gram, or 0.5 per cent.

Mean = 0.69 per cent.

Calcium Carbonate.

- (1.) 7.0409 grams treated with hot water and gently ignited gave 0.0284 gram, or 0.433 per cent.
- (2.) 6.8493 grams treated as above gave 0.0106 gram, or 0.155 per cent.

Mean = 0.294 per cent.

Lead Sulphate.

- (1.) 7.3436 grams treated with a mixture of water and alcohol gave 0.5055 gram on ignition, or 6.88 per cent.
- (2.) 6.8126 grams treated in the same way gave 0.4609 gram, or 6.76 per cent.

Mean = 6.82 per cent.

Barium Sulphate.

- (1.) 6.662 grams treated with hot water and ignited gave 0.1889 gram, or 2.83 per cent.
- (2.) 8.9898 grams treated in the same way gave 0.2138 gram, or 2.39 per cent.

Mean = 2.61 per cent.

Strontium Sulphate.

- (1.) 8.1265 grams treated with water and alcohol, and allowed to stand 24 hours, &c., gave 0.1484 gram on ignition, or 1.8 per cent.
- (2.) 5.9489 grams treated in the same manner as above gave 0.1129 gram, or 1.89 per cent.

Mean = 1.845 per cent.

Calcium Sulphate.

- (1.) 7.8478 grams dissolved in water, precipitated by ammonium oxalate and ammonia, &c., and ignited over blowpipe, gave 0.048 gram oxide, equivalent to 0.1165 gram sulphate, or 1.484 per cent.
- (2.) 5.6308 grams treated in the same manner gave 0.0341 gram oxide, equivalent to 0.08281 gram sulphate, or 1.47 per cent.

Mean = 1.477 per cent.

Neutral Lead Chromate.

- (1.) 8.3602 grams, treated with hot water, filtered through weighed filter, and dried at 100°, gave 0.0168 gram, or 0.194 per cent.

- (2.) 5.7933 grams treated in same way gave 0.0171 gram, or 0.295 per cent.

Mean = 0.245 per cent.

Neutral Barium Chromate.

- (1.) 6.7173 grams dissolved in water, a little hydrochloric acid added, precipitated by sulphuric acid, &c., gave, on ignition, 0.0138 gram sulphate, equivalent to 0.0149 gram chromate, or 0.22 per cent.
- (2.) 9.3659 grams treated in same way gave 0.0163 gram sulphate, equivalent to 0.0177 gram chromate, or 0.19 per cent.

Mean = 0.205 per cent.

Neutral Strontium Chromate.

- (1.) 8.5477 grams dissolved in water, precipitated by sulphuric acid, alcohol being added, allowed to stand 24 hours, &c., gave 0.1391 gram sulphate on ignition, equivalent to 0.1544 gram chromate, or 1.806 per cent.
- (2.) 8.2775 grams treated in same way gave 0.1836 gram sulphate, equivalent to 0.2028 gram chromate, or 2.46 per cent.

Mean = 2.133 per cent.

Neutral Calcium Chromate.

- (1.) 6.1202 grams precipitated as oxalate, weighed as oxide, gave 0.0118 gram oxide, equivalent to 0.0329 gram chromate, or 0.537 per cent.
- (2.) 6.44 grams treated in same way gave 0.0129 gram oxide, equivalent to 0.03598 gram chromate, or 0.557 per cent.

Mean = 0.547 per cent.

The results obtained show that the eutectic alloys of the following salts with sodium nitrate contain the following percentages by weight of the respective salts:—

	Sulphate.	Chromate.	Carbonate.
Barium	2.61	0.205	0.916
Strontium	1.845	2.133	0.69
Calcium	1.477	0.547	0.294
Lead	6.83	0.245	—

The solubility of lead carbonate could not be ascertained on account of its being decomposed at the temperature of fused sodium nitrate.

I may refer here to the corresponding solubilities of a few of these bodies in fused potassium nitrate as given by my father.

Lead sulphate.....	4.61 per cent.
Calcium „	0.93 „
Barium „	0.98 „

XII.—*Note on the Heats of Dissolution of the Sulphates of Potassium and Lithium.*

By SPENCER UMFREVILLE PICKERING, M.A. Oxon., Chemical Lecturer at Bedford College.

THE existence of anhydrous sodium sulphate in two modifications, as shown in a previous communication (this Journal, Trans., 1884, p. 686), rendered it advisable to investigate the sulphates of other alkali metals in a manner similar to that in which the sodium salt had been examined.

Potassium Sulphate.

The following results were obtained with various specimens of this salt, the initial temperature of the calorimetric water being $22.793^{\circ}\text{C.} \pm 0.05^{\circ}$. All the specimens were powdered and sifted through silk. Proportion of water used, 420 H_2O .

Specimen.		Molecular heat of dissolution.
1. Dried over hydrogen sulphate at about 20°		— 6139 cal.
2. Ditto for seven days		— 6174 „
3. Heated at 100° for 19 hours		— 6044 „
4. Heated at 200° for $2\frac{1}{2}$ hours	$\left\{ \begin{array}{l} -6237 \\ -6241 \end{array} \right\}$	— 6239 „
5. Ditto ditto		— 6290 „
6. Heated at a bright red heat for 20 minutes....		— 5168 „
7. Ditto ditto ditto		— 6112 „
Mean.....		— 6167 „

As will be seen, the samples dried at 200° give somewhat higher numbers, — 6256, namely, as a mean, than the others, and it seems preferable to take this number as representing the true heat of dissolution, instead of taking a general mean of all the results, since it was found

that, in spite of the fine state of division to which the salt was reduced, and the long time employed for its desiccation, portions of Nos. 2 and 3, on being heated to redness, decrepitated very slightly, rendering the presence of a small amount of water probable; it is true that the samples which had been heated to redness yielded numbers identical with Nos. 1, 2, and 3, and the only suggestion which offers itself is, that, owing to the high temperature to which they had been exposed, they retained a certain amount of abnormal heat in the same way that a salt which has been fused generally retains some of its heat of fusion. The difference in results, however, is but slight, and even if it were wholly without explanation, would by no means warrant us in concluding that there are modifications of potassium sulphate similar to those of the sodium salt.

Berthelot and Thomsen give — 5950 and — 6010 cal. respectively at 22·8° C., numbers somewhat lower than those given here; but it must be remembered that these chemists use only half the proportion of water (200H₂O) used by myself, and that, therefore, we may expect to find small differences in some cases due to this cause.

Lithium Sulphate.

The only existing determinations of the heat of dissolution of this salt is that of Thomsen, who gives (6054 and 6404) 6229 cal. for the value of the equation $\text{Li}_2\text{SO}_4 + 200\text{H}_2\text{O}$ at 19° C. (*J. pr. Chem.*, 17, 171).

The following are the values which were obtained with different samples at 22·751° C. \pm 0·05°:—

Specimen.	Molecular heat of dissolution.
1. Dehydrated at 100—110° (loses its water very slowly at this temperature)*.....	6467 cal.
2. Dehydrated at 200°	6563 „
3. Dehydrated, and then fused and powdered 12 hours before being dissolved	6512 „
Mean.....	6514 „

Thomsen's determinations reduced to this temperature give 6257 and 6525 cal. respectively.

Here, as in the case of potassium sulphate, we find no evidence of there being more than one modification of the salt.

* Crystallised lithium sulphate ($\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$) does not lose its water of crystallisation when exposed over sulphuric acid at ordinary temperatures.

XIII.—Calorimetric Determinations of Magnesium Sulphate.

By SPENCER UMFREVILLE PICKERING, M.A. Oxon, Lecturer on Chemistry at Bedford College.

THE heat of dissolution of monohydrated magnesium sulphate is given by Graham as 13,200 cal. (*Phil. Mag.*, **22**, 329); by Favre, as 10,986 cal. (*Compt. rend.*, **73**, 1147); and by Thomsen as 13,300 *J. pr. Chem.*, **18**, 5). Graham's determinations must be looked upon with distrust at the present day, and Thomsen regards Favre's numbers as containing some obvious error, which error, however, he does not attempt to explain. Unfortunately none of these chemists give any details as to the preparation or analysis of the salt which they used, and that such details are most necessary has been shown in the previous communications.

Numerous experiments showed plainly that any analysis of magnesium sulphate based on the determination of the sulphur present in it gives utterly false results. When precipitated in the ordinary way by barium chloride, the sulphur trioxide is found to be 1 or 1·5 per cent. too high, in spite of every possible precaution; digestion of the ignited barium sulphate with dilute acid causes a very appreciable amount of barium sulphate to be lost, whilst fusing it with an alkaline carbonate and reprecipitating it involves so many new sources of error as to make the method untrustworthy in a case like this, where a small difference in the percentage of sulphur present would make a considerable difference in the heat of dissolution of two specimens. Again, the methods for the estimation of magnesium are not sufficiently accurate to be used with any success here. The only trustworthy method for ascertaining the composition of any magnesium sulphate is a determination of the percentage of water present in it; this method is rendered easy by the fact that the heptahydrated salt does not effloresce or deliquesce when exposed to air, and loses all its water without any further decomposition when heated to a low red heat. A large quantity of the crystallised salt was powdered very finely, and exposed to air till it remained constant in weight; on heating this over a burner it lost (51·236, 51·171) 51·237 per cent. of water, the theoretical loss being 51·214 per cent.*

* Many other experiments with different samples showed that the crystallised salt after exposure to air corresponded exactly to the formula $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

In these water determinations, as much as 100–200 grams were taken for each analysis, the product of the analysis serving as a preparation for use in the calorimeter. Care must be taken not to stir the dehydrated salt in an open dish while

It is by no means easy to obtain the monohydrated sulphate. When the heptahydrated salt is heated at 100—130° it loses weight very slowly indeed, and after many days it becomes apparently constant in weight, still retaining, however, about $1\frac{1}{3}\text{H}_2\text{O}$; the excess of $\frac{1}{3}\text{H}_2\text{O}$ may be expelled by raising the temperature to 150—160°, but if the temperature rises much above this, some of the anhydrous salt will be formed. Consequently it is impossible to prepare the monohydrated substance at different temperatures, as in the case of sodium sulphate, &c. The only method which suggested itself of ascertaining whether the temperature of preparation affects the constitution of the salt was to prepare samples at different temperatures and make corrections for the small excess or deficiency of water present in them.

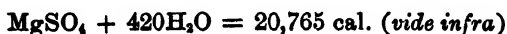
The following table embodies the results obtained with four different preparations. The temperature of the calorimetric water was $22.183^\circ \pm 0.06$; and the proportion of it $420\text{H}_2\text{O}$. In experiments with hydrated salts, the water of hydration is reckoned as so much calorimetric water:—

Temperature at which pre- pared.	Loss of water during preparation.	Molecular heat of dissolution.	
		Observed.	Corrected accord- ing to the loss of water.
1. 165° C.	44.013 per cent.	$\left\{ \begin{array}{l} 12,366 \\ 12,428 \end{array} \right\}$ 12,397 cal.	12,260 cal.
2. 155 „	43.889 „	$\left\{ \begin{array}{l} 12,041 \\ 11,997 \end{array} \right\}$ 12,019 „	12,023 „
3. 135 „	43.049 „	$\left\{ \begin{array}{l} 11,826 \\ 11,831 \end{array} \right\}$ 11,829 „	12,139 „
4. 115 „	43.155 „	$\left\{ \begin{array}{l} 11,877 \\ 11,755 \end{array} \right\}$ 11,833 „	12,104 „
	Theoretical loss for $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ to $\text{MgSO}_4 \cdot \text{H}_2\text{O}$. 43.898 per cent.	Mean.....	12,131 „

Two different samples were used for making these four preparations.

In order to make the corrections contained in the above table, it was necessary to know the heat of dissolution of the heptahydrated and anhydrous salts under like conditions. My determinations of these quantities were as follows:—

hot, since its state of division is so fine that ascending currents of hot air will cause a certain amount of loss mechanically.



$$\text{and } \text{MgSO}_4 \cdot 7\text{H}_2\text{O} + 420\text{H}_2\text{O} = \left\{ \begin{array}{l} -3877 \\ -3963 \\ -3904 \end{array} \right\} -3915 \text{ cal.}$$

Where the samples contained an excess of water over H_2O , it is assumed that the other six molecules of water are all combined with the same energy; this is very probably not the case, but, as will be shown below, it is the only safe ground on which to introduce any correction at all, though, by so doing, we may not obtain such concordant numbers as we might if we knew the exact state of the case; still, the numbers which are thus obtained are sufficiently concordant to show that the monohydrated salt dissolves with the same heat evolution (12,131 cal.*) when prepared at any temperature within the possible range; that there is but one modification of this salt, and that, therefore, we must seek some other explanation of the discordant results obtained by Favre and Thomsen.

Magnesium sulphate, which had been dried at 130° , and apparently had become constant in weight at that temperature, would yield a number identical with that given by Favre (10,986 cal.), and it would, moreover, on a determination of the sulphur trioxide in the ordinary way, appear to correspond exactly to $\text{MgSO}_4 \cdot \text{H}_2\text{O}$, although in reality, it still retained about $1\frac{1}{2}\text{H}_2\text{O}$. Favre's results, therefore, are easily explained by supposing him to have prepared his salt in such a way.

Thomsen's number, 13,300† cal. at 17° , on the other hand, exceeds that here given, and may be explained by his having employed too high a temperature for the desiccation of the salt, and having thereby obtained a preparation which, though it might contain the exact quantity of water, consisted in reality of a certain amount of the anhydrous salt mixed with some hydrated salt containing more than H_2O . From the very small range of temperature at which the monohydrate may be obtained without decomposition, such an explanation appears very probable; and by no means less so when we consider the rest of Thomsen's work on this salt.

This work consisted of an attempt to determine the heat of combination of the various molecules of water in the salt $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, by ascertaining its heat of dissolution when dehydrated to various extents. In no case was any definite hydrate obtained, but the heat of dissolution of $\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$, for instance, was deduced from experi-

* In comparing the individual experiments, it must be remembered that the corrected results depend not only on the calorimetric determinations, but also on the accurate estimation of the small excess or deficit of water present.

† He deduces this number from a preparation having the composition $\text{MgSO}_4 \cdot 1.102\text{H}_2\text{O}$.

ments with samples having the composition $\text{MgSO}_4 \cdot 5 \cdot 056\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 5 \cdot 065\text{H}_2\text{O}$. Now it is only necessary to look at any partially dehydrated salt to become convinced that it is certainly not a homogeneous mixture; that when, say, it corresponds in weight to $\text{MgSO}_4 \cdot 3\text{H}_2\text{O}$, it is in reality a mixture of the monohydrated salt with particles retaining a much larger proportion of water, and that experiments with it would throw no light whatever on the behaviour of the hydrate $\text{MgSO}_4 \cdot 3\text{H}_2\text{O}$.* Where, as in Thomsen's experiments with sodium sulphate, any loss of water causes a proportional increase in the heat of dissolution, we may safely conclude that all the molecules of water present are combined with the same energy; where, however, as in the case of magnesium sulphate, no such proportionality is found, the only conclusion which can be drawn is that all the molecules of water have not the same value.†

Anhydrous Magnesium Sulphate.

Two different specimens of the anhydrous salt prepared at a very low red heat gave the following results at $22 \cdot 183^\circ$ when dissolved in $420\text{H}_2\text{O}$:—

A.	$\left\{ \begin{array}{l} 20,731 \\ 20,765 \end{array} \right\}$	mean	20,748 cal.
B.	$\left\{ \begin{array}{l} 20,745 \\ 20,820 \end{array} \right\}$	„	20,782 „
			20,765 „

numbers practically identical, and agreeing very well indeed with Thomsen's 20,797 cal. (reduced to the same temperature), and from which we may conclude that there is no evidence of the existence of more than one modification of anhydrous magnesium sulphate.

It is true that Berthelot (*Ann. Chim. Phys.*, 29, 305) with a sample which had been heated to 320° only found 19,190 cal. (at $22 \cdot 183^\circ$), but on repeating this experiment at even a lower temperature (250°) the author of the present paper obtained the number 20,825 cal., which would indicate that Berthelot's preparation was not quite anhydrous.

The different manner in which the anhydrous and monohydrated

* Such a statement would naturally not apply to salts obtained by the special methods employed by Thorpe and Watts (*Abstr.*, 1880, 102) for the preparation of some of these hydrates.

† In Thomsen's experiments the initial temperature of the calorimetric water ranges from $15 \cdot 5$ — $18 \cdot 6^\circ$, a range sufficiently large to introduce great errors in the values obtained. The general conclusions which he draws would also be much modified by the value here given for the heat of dissolution of the monohydrate.

salts dissolve in water is worthy of notice; the former cakes, but dissolves quickly when pounded up in the water, whereas the latter does not cake, but takes about ten minutes to dissolve, rendering the water milky meanwhile. This shows that the monohydrate cannot be formed as the first product of the hydration of the anhydrous sulphate.

XIV.—On certain Derivatives of Isodinaphthyl.

By ADOLF STAUB, Ph.D., and WATSON SMITH, Lecturer in Technological Chemistry in the Owens College, Manchester.

IN a paper by one of us, read before the Chemical Society in the autumn of 1877 (this Journal, 1877, ii, 564), it was stated that possibly "by gentle oxidation of the dinaphthyls the corresponding isomeric naphthoic acids may be obtained. One might, for example, expect to get from α - α -dinaphthyl, α -naphthoic acid, from β - β -dinaphthyl, β -naphthoic acid, whilst α - β -dinaphthyl might probably yield a mixture of these naphthoic acids."

Experiment has shown us recently that isodinaphthyl, which must be either β - β - or α - β -dinaphthyl—most probably the former—is by no means amenable to gentle oxidation so as to yield the desired results, for when treated in the cold with strong nitric acid a nitro-product was obtained, and if heated with dilute nitric acid (sp. gr. = 1.25) in sealed tubes at 150° to 170°, the whole of the substance was oxidised, forming phthalic acid. Again, by boiling the dinaphthyl with a neutral aqueous solution of potassium permanganate for about 12 hours, only a small portion became oxidised, but here again phthalic acid was formed, and it was easily detected by the formation of a white precipitate with barium nitrate in ammoniacal solution, and by conversion into the anhydride.

In this experiment, the greater part of the dinaphthyl remained unattacked by the oxidising agent. In another experiment, the dinaphthyl was treated with a solution of chromic acid in glacial acetic acid. Partial oxidation ensued, with formation of a quinone.

Isodinaphthyl-quinone, C₂₀H₁₀O₄.

In order to prepare and isolate this quinone, 10 grams of the dinaphthyl were dissolved in warm glacial acetic acid and added to a similar solution of 31 grams of chromic anhydride (i.e., double the

quantity theoretically required). After some time, the solution was warmed on the water-bath to complete the reaction as far as possible, and the warm liquid was then poured into from five to six times its volume of water. The impure quinone was thus obtained as a brownish-yellow voluminous precipitate, which after being thoroughly washed with water was pressed between blotting-paper and dried. The yield was a very poor one, viz., about 0.5 gram of pure quinone from the 10 grams of dinaphthyl taken, or 5 per cent. This quinone was repeatedly crystallised from benzene and from glacial acetic acid, in order to free it from adhering traces of chromic oxide and isodinaphthyl. The pure quinone is a yellow amorphous powder, sparingly soluble in the best solvents; the most suitable appeared to be glacial acetic acid. When heated in a capillary tube, it turns brown at 215°, and melts with decomposition between 250° and 260°.

Analysis by combustion furnished the following results:—

- (1.) 0.2212 gram of substance gave 0.6165 gram CO_2 and 0.0744 gram H_2O .
- (2.) 0.1795 gram of substance gave 0.5042 gram CO_2 and 0.0560 gram H_2O .

	Found. Per cent.		Calculated for $\text{C}_{20}\text{H}_{10}\text{O}_4$ Per cent.
	(1.)	(2.)	
C	76.01	76.64	76.43
H	3.74	3.53	3.18

When heated with alkaline solutions, small quantities of the substance were dissolved, yielding a wine-red solution. On adding acids to this solution, a roddish-brown powder was precipitated. The quantity obtained was too small for analysis or further examination. If the quinone is boiled for several hours with alcohol, it turns brown, probably from the formation of the quinhydrone.

Tetranitro-isodinaphthyl, $\text{C}_{20}\text{H}_{10}(\text{NO}_2)_4$.

10 grams of isodinaphthyl were gradually introduced into 120 parts of nitric acid of sp. gr. about 1.5, the action being checked by cooling if necessary. When the action was nearly finished, the mixture was heated on the water-bath in order to complete it and bring all the substance into solution. The warm solution was then poured into a large excess of water, whereby the nitro-compound was thrown down as a yellow flocculent precipitate. If the quantity of water was too small, or if it was warm, the precipitate was more or less resinous. The flocculent precipitate was next washed well, and

then dried in a vacuum in the exsiccator. After drying, it was dissolved in absolute alcohol, and the alcoholic solution was very slowly cooled to prevent the separation of the nitro-compound in the resinous form. Thus prepared, it was obtained as an amorphous brownish-yellow powder, sparingly soluble in all solvents. The best of these is concentrated nitric acid, and from the solution it is precipitated by water in yellow flocks. It melts with decomposition at about 150° . If heated up quickly, it suddenly decomposes with a slight explosion, and leaves a carbonaceous residue like most other organic nitro-compounds.

By analysis, the following data were obtained:—

- (1.) 0.2348 gram of substance gave 0.4810 gram CO_2 and 0.0602 gram H_2O .
- (2.) 0.1990 gram of substance gave 0.4006 gram CO_2 and 0.0477 gram H_2O .
- (3.) 0.2486 gram of substance gave 26.5 c.c. N at 769 mm. bar. and 17° .
- (4.) 0.2295 gram of substance gave 0.4638 gram CO_2 and 0.0555 gram H_2O .

	Calculated for $\text{C}_{20}\text{H}_{10}(\text{NO}_2)_4$. Per cent.	Found.			
		(1.)	(2.)	(3.)	(4.)
C	55.30	55.87	54.90	—	55.12
H	2.30	2.85	2.66	—	2.68
N	12.90	—	—	12.52	—

The solution of this tetranitro-compound, when treated with acetic acid and zinc-dust, yields the corresponding amido-compound, which separates out from the solution as a bluish-grey flocculent precipitate, readily oxidised on exposure to the air.

Tetramido-isodinaphthyl, $\text{C}_{20}\text{H}_{10}(\text{NH}_2)_4$.

This derivative was obtained by adding to a solution of the tetranitro-compound in glacial acetic acid, zinc-dust in small quantities at a time, and heating on the water-bath so as to complete the reaction. On filtering from the excess of zinc-dust and pouring the solution into excess of water, the amido-compound separated out in the flocculent form.

After collecting the substance and drying* in a vacuum, it was recrystallised from pure toluene. Thus purified, the amido-compound

* If not completely dry, it is difficult to prevent the assumption of a resinous character on recrystallising from toluene.

was obtained as a slightly grey-coloured powder, almost amorphous in character. It is sparingly soluble in alcohol, but somewhat more easily in toluene and in glacial acetic acid. When heated in a capillary tube, it began to turn brown at 150° , and melted at 164° to 167° , while gradually decomposing. A nitrogen determination gave the following results:—

0.1603 gram of substance yielded 24.1 c.c. N. at 21° and 764 mm. bar.

	Calculated for $C_{20}H_{10}(NH_2)_4$. Per cent.	Found. Per cent.
N	17.83	17.60

The compounds of this remarkably stable dinaphthyl so far obtained are as follows:—

Tetrachlor-isodinaphthyl	$C_{20}H_6Cl_4$.
Heptabrom-isodinaphthyl	$C_{20}H_4Br_7$.
Isodinaphthyl-monosulphonic acid..	$C_{10}H_7.C_{10}H_4.SO_3H$.
Calcium isodinaphthyl-monosulpho- nate	$(C_{10}H_7.C_{10}H_4.SO_3)_2Ca + 2H_2O$.
Barium isodinaphthyl-monosulpho- nate	$(C_{10}H_7.C_{10}H_4.SO_3)_2Ba + 2H_2O$.
Barium isodinaphthyl-disulphonate	$(C_{10}H_4SO_3)_2Ba + xH_2O$.
Lead isodinaphthyl-disulphonate ..	$(C_{10}H_4SO_3)_2Pb + xH_2O$.
Lead isodinaphthyl-tetrasulphonate	$C_{10}H_4(SO_3)_4Pb$ $C_{10}H_4(SO_3)_4Pb + 6H_2O$.
Isodinaphthylquinone	$C_{20}H_6O_4$.
Tetranitro-isodinaphthyl	$C_{20}H_6(NO_2)_4$.
Tetramido-isodinaphthyl	$C_{20}H_{10}(NH_2)_4$.

A phenol and a cyanogen-compound have also been prepared in small quantity, but they have not, as yet, been quantitatively examined.

XV.—On the Atomic Weight of Titanium.

By T. E. THORPE, F.R.S., Professor of Chemistry in the Yorkshire College, Leeds.

THE existence of the element we now call titanium was first made known in 1789 by Mr. W. Gregor: he found it in the titaniferous iron-sand in the bed of a small stream near Menaccan, in the parish of St. Keverne, in Cornwall. Hence the mineral became known as *menacconite*, and the metal as *menachin*.

In 1793, Klaproth detected the new element in a specimen of red schorl from Hungary, and, in ignorance of Gregor's discovery, he termed the metallic radicle *titanium*. His experiments were repeated and confirmed by Vauquelin and Hecht in 1796. Klaproth subsequently examined *menacconite*, and found that *menachin* and titanium were identical.

Although titanium is usually regarded as a comparatively rare element, its atomic weight was made the subject of investigation as far back as 1823. In that year, Heinrich Rose published a series of determinations based upon the conversion of titanium disulphide into the dioxide by heating it in a current of air, but the results were recognised by Rose himself as unsatisfactory owing to the difficulty of preparing the sulphide pure—that is, free from admixed oxide. The attempt was made to correct for the possible error by heating the sulphide in chlorine gas and weighing the residual titanic oxide, but the numbers were too discordant to permit of the deduction of any accurate value for the atomic weight. (*Gilbert's Annalen*, 73, 155.)

In 1829, Rose (*Pogg. Ann.*, 15, 145) made known the results of his analyses of titanium tetrachloride, a substance first obtained by Mr. E. S. George, of Leeds, by heating the cyanonitride of the blast furnaces in a stream of chlorine (*Thomson, Ann. Phil.*, 9, 1825, 18—20). The chloride was prepared by Rose by heating a mixture of the dioxide and charcoal in chlorine, and was rectified by boiling first over mercury and then over potassium. The portion selected for analysis was distilled four or five times; it was perfectly clear, and gave no indications of free chlorine on decomposition with water. Weighed portions of the chloride contained in small glass bulbs were broken under water in a stoppered bottle, the milky solution was diluted with water and mixed with a very slight excess of ammonia. The titanic acid was separated by filtration and weighed; the filtrate was gently heated to expel the free ammonia, acidulated with nitric acid, mixed

with silver nitrate, and the silver chloride filtered off and weighed. In all, five experiments were made on quantities varying between 0.885 gram and 3.0455 grams.

Rose does not explicitly state what numbers he adopts for the atomic weights of silver and chlorine, but inasmuch as he regards 74.46 of chlorine (the percentage amount of that element found by him in what he considered as the most trustworthy experiments) as equivalent to 16.82 of oxygen, Cl would be 35.4 if O were 16; and since it appeared that 1 gram of titanium tetrachloride yielded 3.0184 grams silver chloride, it follows that Ag was regarded as 108.1.*

The percentage amounts of chlorine obtained in the five experiments were respectively—

74.18; 74.43; 74.37; 74.51; 74.53.

Rose, however, rejects the first result, on the ground that it was obtained from a relatively small quantity of material, and takes the mean of the others: hence the percentage composition becomes—

Chlorine.....	74.46
Titanium.....	25.54
	<hr/>
	100.00

and since, according to Rose, 74.46 parts of chlorine are equivalent to 16.82 parts of oxygen, it follows that the percentage composition of titanium dioxide is—

Titanium.....	60.29
Oxygen	39.71
	<hr/>
	100.00

The determinations of the amount of titanic oxide directly obtained indicated that 100 parts of the tetrachloride gave respectively the following quantities of the dioxide:—

42.83; 42.48; 42.66; 43.42; 43.27.

Rose selects the first three numbers, of which the mean is 42.657, and from these he calculates the percentage amount of oxygen in the dioxide as 40.12; if the mean of the whole be taken it becomes 41.35.

These results have been discussed by Becker ("Smithsonian Collections," 1880, 123); by F. W. Clarke ("Smithsonian Collections," 1882, 207); and by Meyer and Seubert ("Atomgewichte der Elemente, &c." Breitkopf and Härtel, Leipzig, 1883). According to Clarke, Rose's numbers afford the following values for Ti:—

* The accepted ratios of O : Cl : Ag at that time were 100 : 221.325 : 1351.807.

" From percentage amount of TiO_2 ..	$\text{Ti} = 50.493 \pm 0.410$
" $\text{AgCl} : \text{TiCl}_4$	$\text{Ti} = 48.232 \pm 0.127$
" $\text{AgCl} : \text{TiO}_2$	$\text{Ti} = 49.523 \pm 0.206$
$\text{H} = 1, \text{O} = 15.9633, \text{Cl} = 35.37, \text{Ag} = 107.675$ "	

Rose himself, it should be stated, rejects the values obtained from the amount of titanic oxide, on the ground that this compound does not afford a trustworthy basis for the estimation, by reason of its hygroscopic character which prevents an accurate determination of its weight.

Meyer and Seubert, who employ the ratios—

$$\text{O} : \text{Cl} : \text{AgCl} = 1 : 6.7456 : 8.96146,$$

calculate from the sums of the weights of TiCl_4 , TiO_2 , and AgCl in the several experiments—

$$\text{TiCl}_4 : \text{O} = 11.879 : 1 \text{ (min. } 11.866; \text{ max. } 11.891)$$

$$\text{TiO}_2 : \text{O} = 5.106 : 1 \text{ (min. } 4.932; \text{ max. } 5.152).$$

On the assumption that $\text{H} = 1$ and $\text{O} = 15.96$; the mean results give respectively—

$$\text{TiCl}_4 : \text{AgCl} \quad \text{Ti} = 48.13 \text{ (min. } 47.92; \text{ max. } 48.32)$$

$$\text{TiO}_2 : \text{AgCl} \quad \text{Ti} = 49.58 \text{ (min. } 46.80; \text{ max. } 50.30).$$

There are several possible sources of error in the method employed by Rose. In the first place, repeated distillation of the tetrachloride in air leads to the formation of small quantities of Troost and Hautefeuille's oxychloride; and in the next, owing to the great care taken to avoid excess of ammonia, the precipitated oxide might well contain basic chlorides, analogous to the chlorostannic acid of Mallet, or Ti_2OCl_2 , corresponding to stannous oxychloride. It will be shown further on that the precipitated oxide is very apt to retain traces of chlorine which are expelled as tetrachloride on heating, unless it is repeatedly treated with solution of ammonia.* Moreover, prolonged and intense ignition is required to obtain the dioxide absolutely anhydrous. The final mean from Rose's numbers will also be slightly affected by the circumstance that his weighings were not reduced to a vacuum standard.

In 1830, Mosander (*Pogg. Ann.*, 19, 212) published a series of numbers showing the percentage amount of oxygen in titanic oxide. No details are given, but the estimations are most probably based upon the decomposition of the tetrachloride by water.

* Van Bemmelen's experiments have shown with what tenacity colloidal substances like the hydrated oxides of tin and silicon, bodies analogous to titanium oxide, retain water, acids, and salts (*J. pr. Chem.* [2], 23, 324; 26, 227).

In all, nine determinations appear to have been made; the results varied from 39·830 to 40·825; the mean of the series is 40·428, which gives for Ti 47·04.

In the same year, Dumas (*Ann. de Chim.*, **44**, 288) found the vapour-density of titanium tetrachloride to be 6·836 (air = 1) from which if Cl = 35·4, Ti becomes 55·6. Of course this result has no other value than as serving to determine the molecular formula of the chloride. The errors incidental to the method, especially in the case of such a body as titanium tetrachloride, would certainly tend to give too high a value for the density, and hence for the atomic weight of titanium.

The determinations which have hitherto been deemed most trustworthy are those of Pierre, made in 1847 (*Ann. de Chim.* [3], **20**, 257): on these, the value for Ti given in the greater number of the text-books is based. Pierre, who had prepared a quantity of the tetrachloride for the purpose of studying its thermal expansion, made a number of estimations of the amount of chlorine contained in it by the method of Gay-Lussac. The chloride was obtained from the artificial oxide and was free from iron. According to Pierre, it could hardly have contained silicon chloride, as the first portions of the distillate were rejected, and its boiling point was perfectly constant. Weighed portions of the chloride, in quantities varying from 0·6325 gram to 0·8215 gram, were broken under water in well-stoppered bottles, and the chlorine in the solution was determined by the addition of a standard solution of silver. The results of the whole of the observations (nine in number) gave for Ti 49·889. Pierre, however, was inclined to believe that only the first three results, which agreed fairly well together, were trustworthy, and he accordingly rejects the other six, which gave lower values for Ti, on the ground that the chloride had been affected by atmospheric moisture. The first three give Ti, 50·259 (O = 15·963; Cl, 35·37; Ag, 107·675); or, adopting Meyer and Seubert's ratios, we have—

$$\begin{aligned} \text{TiCl}_4 : 4\text{Ag} &= 2\cdot3730 : 5\cdot33045 \\ &= 1\cdot7807 : 4 \\ \text{TiCl}_4 : \text{O} &= 12\cdot012 : 1 \\ \text{Ti} : \text{O} &= 3\cdot149 : 1 \\ \text{Ti} : \text{H} &= 50\cdot25 : 1 \end{aligned}$$

Pierre's results, it will be seen, differ by more than two units from those Rose obtained by weighing the silver chloride. This may be accounted for by loss of chlorine in the act of solution, by the possible presence of oxychloride, or by the coprecipitation of basic chloride, all of which circumstances would tend to decrease the amount of silver needed for complete precipitation, and hence raise

the value of Ti. The quantities of the chloride taken for analysis (on the average about 0.8 gram) were scarcely sufficient for the purpose of an accurate determination of atomic weight.

The only other contribution to our knowledge of this subject is due to A. Demoly (*Compt. rend.*, par Laurent et Gerhardt, 1849, 326; *Ann. Chem. Pharm.*, 72, 213). Rutile containing iron, manganese, and silica was mixed with charcoal and heated in chlorine, and the chlorides were distilled from mercury and potassium. In order to free this product from silicon tetrachloride (which Demoly assumed must have been present in the preparations employed by Rose and Pierre), it was treated with gaseous ammonia and converted by ignition into the nitride. This was then heated in chlorine gas and the chloride was distilled through a system of bulbs connected together by grinding and containing mercury, potassium-amalgam, and potassium. The method of analysis was identical with that of Rose. The following were the results:—

TiCl_4 .	AgCl.	TiO_2 .
1.470 grams gave	4.241 grams and	0.565 gram
2.330 "	6.752 "	0.801 (? 0.901)
2.880 "	8.330 "	1.088 "

From these numbers, Demoly calculates the composition of titanium tetrachloride as follows:—

Chlorine	72.02
Titanium	27.98

100.00

The atomic weights of chlorine and silver adopted in the calculation are not stated, but from the amount of silver chloride furnished by 100 parts of the tetrachloride, Demoly arrives at the value $\text{Ti} = 56$.

Demoly, however, appears to have ignored the fact that his analytical results afford several ratios from which three independent values for the atomic weight of titanium can be deduced. These values have been calculated by Clarke (*loc. cit.*, 210) with the following results:—

" From per cent. of TiO_2	$\text{Ti} = 36.063 \pm 0.519$
" AgCl : TiO_2	$\text{Ti} = 43.841 \pm 0.350$
" AgCl : TiCl_4	$\text{Ti} = 56.386 \pm 0.181$
General mean....	52.191 ± 0.153 "

These results enable us to form an idea of the character of the

product analysed by Demoly. It may be remarked in passing that the precise practical value of calculating their "probable errors" or of taking a "general mean" is not very apparent. The editor of the *Annalen* (*loc. cit.*) contents himself with remarking:—"Dieses Resultat (56) weicht so bedeutend von demjenigen ab, welches H. Rose and Pierre nach ähnlichem Verfahren erhielten, dass zur Feststellung dieses Aequivalente neue Versuche erforderlich sind." This conclusion will be sufficiently obvious from the foregoing statement of what is to be found in the literature of the subject. Professor Clarke (who includes Demoly's numbers in his final mean) concludes that the atomic weight of titanium is "imperfectly determined;" and Meyer and Seubert place it in the list of those elements of which the value is uncertain to within several units.

In framing his arrangement of the elements in accordance with the Periodic Law, Mendelejeff adopted the number 48 as the atomic weight of titanium. A number less than 50 was in fact demanded by the law. Mendelejeff says: "Zugleich ist auf Grund des periodischen Gesetzes anzunehmen dass die Zahlen von Pierre und Demoly höher als die wirklichen sind; denn das Atomgewicht von Ti muss um ein Geringes bloss höher sein als $\text{Ca} = 40$, und kleiner als $\text{V} = 51$ und $\text{Cr} = 52$. Daher ist die Zahl von Rose am wahrscheinlichsten, während das Titanchlorid der anderen Forscher geringe, das Atomgewicht erhöhende Verunreinigungen erhalten hat." Mendelejeff, in fact, ventures to suggest that the titanium chloride of the French observers may have contained the chloride of the missing element *ekasilicium*, the atomic weight of which should be about 72, and the oxide of which should be EsO_2 . "Im äusseren Ansehen, wahrscheinlich auch in den Krystallformen, in den Eigenschaften und in den Reactionen wird dasselbe TiO , nahe stehen." According to Mendelejeff, *ekasilicium chloride*, EsCl_4 , should be a liquid boiling at about 100° , and might therefore be separated from TiCl_4 , which boils at about 136° by fractional distillation; its sp. gr. should be about 1.9, whereas that of TiCl_4 is 1.76. "Doch hat ein von mir angestellter Versuch in TiCl_4 keinen Gehalt von unter 135° siedenden Köpern gezeigt." It is equally certain that the chloride of Pierre contained no sensible quantity of any substance boiling at so low a temperature as 100° , and of a sp. gr. of 1.9. He states that his titanium chloride had a constant boiling point of 136° at 762.3, and that its sp. gr. was 1.76088 at 0° , numbers agreeing closely with those found for this substance in the course of my work on Specific Volumes of Liquids (*Jour. Chem. Soc., Trans.*, 1880), viz., 136.41° and 1.76041 at 0° ; and as will be shown hereafter, so far as regards the boiling point, with that of the chloride which has served for the present investigation. The chloride employed by Demoly also boiled steadily at 135° , and his

determinations of the oxide obtained by decomposing the product with water and dilute ammonia, afford direct evidence that his chloride contained no element capable of forming a dioxide, stable on ignition, and of an atomic weight so high as 72.

The exact determination of the atomic weight of titanium is rendered difficult by the circumstance that comparatively few compounds of this element exist which are wholly suitable for the purpose. It will have been noticed that all the determinations hitherto published have been made on the tetrachloride—a liquid which is not easily obtained free from hydrochloric acid on account of the readiness with which it suffers alteration in contact with moisture. Moreover, it is liable to contain other chlorides, and possibly also oxychlorides. It has been suggested that the titanofluorides might afford the basis of a series of determinations, but both the preparation and analysis of these bodies offer special difficulties. It is true that Marignac has employed the oxyfluorides and fluorides for the estimation of the atomic weights of niobium, tantalum, and zirconium, but the analytical methods were necessarily somewhat complicated and the source of many possible errors; thus, in the case of the potassium tantalofluoride the values for Ta differ among themselves by nearly three units.

The compound selected as the basis of an atomic weight determination should be simple in its nature; it should, of course, contain no other element of uncertain atomic weight, and it should be capable of experiencing a definite chemical change by an operation of the simplest possible character. I made a number of trials at the outset of this investigation in the hope of discovering such a method. The conversion of titanium dioxide into the sesquioxide by intense heating in hydrogen suggested itself. Although the accounts given by Rose and Ebelmen of the difficulty of such conversion afforded little hope of success, several attempts were made to effect the reduction, but the loss of weight, even after prolonged ignition in a porcelain tube at the highest temperature of a small blast-gas furnace, was much less than that demanded by theory. Thus, in the experiment in which the greatest amount of reduction occurred, 0.7645 gram of pure titanicoxide, after being heated to whiteness for nearly two hours in a current of dry hydrogen, lost only 0.0276 gram or 3.6 per cent., whereas the theoretical loss should be about 10 per cent. Subsequent and more prolonged heating occasioned a loss of a few additional milligrams. There was obviously no certain indication that complete reduction to the sesquioxide could be obtained.

I next sought to prepare the disulphide according to Ebelmen's method, with a view of roasting it to the dioxide, as originally sug-

gested by Rose, but although these attempts led to the discovery of certain new sulphides of titanium, they failed to afford a satisfactory process for the determination of the atomic weight of the element, owing mainly to the difficulty of obtaining these bodies in a sufficiently definite form and unmixed with one another.

Attempts to expel the acid radicles, CO_2 and SO_2 , from a number of their salts by titanous oxide, at regulated temperatures, were equally unsatisfactory. It was hoped that the following method might afford a trustworthy basis for a determination. Two platinum crucibles of equal size and weight, each containing about the same weight of recently ignited sodium carbonate, were weighed one against the other. Into one of the crucibles was placed a known quantity of pure titanous oxide, which was carefully mixed with the sodium carbonate by means of a platinum wire. The two crucibles were then placed side by side in a muffle, heated by gas to a bright red heat, and after cooling they were again weighed. From the ratio wt. of CO_2 : wt. of TiO_2 = mol. wt. CO_2 : mol. wt. TiO_2 , the value of Ti might be deduced. The idea, however, came to nothing, since it was found that two approximately equal quantities of sodium carbonate when subjected under similar conditions to a bright red heat for equal times, could not be depended upon to suffer the same loss of weight to within 2 or 3 mgrms.

I accordingly reverted to the haloid compounds of titanium, and of these I finally made use of the tetrachloride and tetrabromide. The tetraiodide I deemed unsuitable on account of the slight decomposition to which it is liable at the high temperature of its boiling point. One objection may possibly be raised against the choice of these bodies. It has been repeatedly pointed out that the only certain criterion of the validity of any atomic weight is that it is based upon the concordant results of completely independent methods of analysis. It may be urged that the analyses of bodies of analogous composition, by methods very similar in character, cannot afford such a criterion. I apprehend, however, that in this particular case the objection has very little practical weight. The tetrachloride and tetrabromide of titanium are really very dissimilar bodies; thus, they are not equally susceptible to alteration either by moisture or by the action of oxygen at a high temperature, and they behave very differently on decomposition with water, a matter of considerable practical importance in their analysis. Moreover, the determinations of the exact amount of the halogens in the two bodies are based upon really independent methods, and the values of Ti which they afford are referred to atomic weights which are themselves obtained by methods equally independent. Indeed, as is well known, there are few atomic weights of which the values are known to such a high degree of precision as

those of silver and the halogens. The determination of the amount of titanic oxide yielded by known weights of the chloride and bromide not only offers the possibility of a second and independent value, but also affords a stringent check upon the purity of these compounds. And lastly, the ratio of the weight of silver used to that of the silver chloride and silver bromide obtained, affords an additional guarantee both of the purity of the silver and of the absence of coprecipitated titanic oxide.

Before describing the modes of preparing and analysing the chloride and bromide of titanium, it may be desirable to give some details respecting the method of weighing and the preparation of the silver employed.

Method of Weighing.—The balance was a short beamed instrument of the Bunge pattern made by Oertling. It was carefully adjusted, and its sensibility under varying loads ascertained by the method of vibrations. The results were as follows:—

Load in grams.	d in mgrms.	Load in grams.	d in mgrms.
0	0.16	20	0.246
2	0.19	50	0.304
5	0.196	100	0.395
10	0.217		

During the day's work the position of equilibrium of the beam of this instrument was subject to a steady progressive alteration, as if the two arms expanded unequally, or as if one became warped during the day, but assumed its original form when the balance was allowed to remain at rest. The extent of the variation was too small to affect the results to any appreciable amount; in practice, the effect was eliminated by taking the position of rest before and after the weighing. The degree of variation may be seen from the accompanying example, taken from a large number of similar observations, made with a view of ascertaining the cause of the phenomenon:—

Oct. 17th, 1881.

Time.	Position of rest.	Time.	Position of rest.
10 A.M.	12.68	1 P.M.	11.23
11 „	12.22	2 „	10.65
12 noon	11.70	3.5 P.M.	10.22
		3.35 „	10.10

The balance case in these observations, as in all subsequent weighings, was shielded from draughts by screens: thermometers placed on each side of the case indicated no difference in temperature. The temperature of the room seldom varied more than 5° during the day, and on some days the variation was much less. No connection was

noticed between the extent of the variation of temperature and the degree of alteration in the position of rest. On the conclusion of the foregoing readings, the balance case was placed at right angles to its former position, and it was allowed to remain at rest for about 18 hours, when the following readings were taken :—

Oct. 18th, 1881.

Time.	Position of rest.
10·15 A.M.	12·27
11	11·83
11·50	11·16
12 noon	11·08
2 P.M.	9·81

During the night, the balance came back to about its original position of rest; as the day advanced, the position of equilibrium gradually altered, as if the left arm had a higher coefficient of expansion than the other, or as if a constant current of air had been set up in the balance case, tending to make one pan appear lighter than the other. This progressive alteration in the position of the zero has been noticed by others: it is particularly mentioned by Miller in his "Determination of the Standard Pound," and I am informed by Professor Poynting that it was constantly observed by him in the course of his observations on the determination of the mean density of the earth by means of the balance (*Proc. Roy. Soc.*, 1878).

The weights employed were of strongly gilded brass: they were made by Staudinger of Giessen. They were compared among themselves by the method of vibrations, one of the 10-gram weights being taken as the standard. The relative values may be given here as showing the degree of accuracy to which weights of good construction are ordinarily adjusted :—

D = denomination of weight

W = true relative weight.

D.	W.	D.	W.	D.	W.	D.	W.
100	99·99908	5	5·00003	0·5	0·50000	0·02	0·02003
50	49·99938	2	2·00011	0·2	0·19994	0·01	0·01000
20	19·99978	1	0·99997	0·1	0·09999	0·01	0·01003
10	10·00000	1'	0·99996	0·1'	0·10001	0·01*	0·010036
10'	10·00007	1"	0·99996	0·05	0·04999	0·01*	0·010002

* Riders.

Whenever practicable the correction for displacement of air, which at best is a very uncertain correction, was obviated or rendered as small as possible by using as a tare a vessel of precisely the same size

and character as that employed to contain the substance weighed. Both vessels were treated in exactly the same manner: thus, if one vessel was heated to redness or placed under a desiccator, the tare was similarly treated and at the same time. In this way, the uncertainty of weight arising from the condensation of air or moisture on the surface of the vessel, or the errors which might be due to the varying density of the air from differences in humidity, were eliminated.

The corrections employed for reduction to a standard atmosphere were as follows:—

Per gram of titanium tetrachloride	+	0.000567	gram
„ „ tetrabromide		0.000333	„
„ „ dioxide		0.000133	„
„ silver chloride		0.000070	„
„ „ bromide		0.000067	„
„ metallic silver		nil.	

Preparation of Metallic Silver.—A solution of the so-called “triple crystallised” silver nitrate of commerce was mixed with excess of dilute hydrochloric acid, and the precipitate was repeatedly boiled with strong nitric acid, washed, dried, and reduced by fusion with a mixture of sodium and potassium carbonates. The button of silver was well washed and dissolved in nitric acid, the liquid was diluted to about 7 litres and mixed with a dilute solution of pure hydrochloric acid, and the vessel was set aside in a dark place. The silver chloride was treated with dilute hydrochloric acid, and repeatedly digested with *aqua regia*, and lastly washed with water. It was then transferred to a silver dish and boiled with a solution of pure caustic soda and milk-sugar until a portion of the precipitate was found to be wholly soluble in nitric acid. The grey precipitate of finely-divided silver was well washed and digested with dilute ammonia to remove any undecomposed silver chloride which might possibly remain; on acidulating the decanted solution with nitric acid not the faintest opalescence was perceived. The silver was next washed with a little dilute sulphuric acid, and finally with distilled water and fused on a support of “brasqued” lamp-black. The fusion was effected at the lowest possible temperature, and care was taken so to regulate the current of air that no excess of oxygen was present in the flame; as the buttons cooled they were surrounded by a faintly luminous flame in order to minimise the chance of the occlusion of oxygen. I have not thought it necessary to attempt to determine the amount of oxygen which might be occluded; the quantity, even if as large as that found by Mallet in the silver employed by him in his determination of the atomic weight of aluminium (*Phil. Trans.*, 1880, 3, 1020) would have no appreciable influence on the result. Mallet only obtained from 80

to 35 c.c. of oxygen per kilo. of silver, an amount far less than that obtained by Dumas, who found as much as 160 or 170 c.c.

I am reasonably certain that the metallic silver employed in my determinations was of a high degree of purity, but I do not imagine that it was purer than that prepared by Mallet and by Stas by the same methods. I have assumed therefore that 1 gram of the metal contained 0.99995 gram of real silver.

TITANIUM TETRACHLORIDE.

About a kilogram of titanium tetrachloride was prepared by igniting precipitated titanous oxide (known to be free from iron and silica) mixed with lampblack which had been previously heated to redness in chlorine, in a stream of chlorine gas. The product was boiled for some time to expel excess of chlorine, and was then distilled: it practically all came over between 135° and 136° . It was again distilled in an atmosphere of dry nitrogen gas, when the following observation of its boiling point was made:—

$$T = 135.78^{\circ}; t = 24.1^{\circ}; N = 32; \text{Bar. } 754.5 \text{ at } 10.1^{\circ}.$$

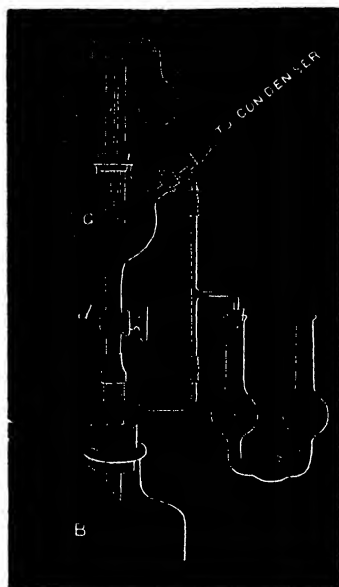
These numbers give $136^{\circ}.35$ at 753.28 mm. for the corrected boiling point. Previous observations (Trans., 1880, 329) gave $136^{\circ}.41$ at 760 mm.

In order to collect portions for analysis without exposure to air, the arrangement shown in Fig. 1, p. 120, was employed.

The air in the apparatus was first removed by a current of dry carbon dioxide, and this gas was then displaced by dry nitrogen. The titanium tetrachloride was transferred to the distilling flask from the bottles in which it had been preserved by replacing the stopper of the bottle by a cork carrying two tubes, one of which ended at the under side of the cork, whilst the other reached to the bottom of the bottle. This latter tube was, outside the bottle, bent twice at right angles, so that the longer limb could be inserted through a perforated cork in the distilling flask. The tetrachloride was then driven over into the flask by the pressure of dry air. The liquid was next distilled, the first portion passing direct into the bottle B, the cock *d* being open. When about one-third of the liquid had passed over, *d* was turned, and the bottle B replaced by a small distilling flask. The cock was again opened and the TiCl_4 allowed to flow into the flask. The distillation was proceeded with until the small distilling flask was almost full. The process was then stopped, and the large distilling flask was replaced by the smaller flask, the bottle B being again placed in its original position. A current of dry nitrogen was again passed through the whole apparatus, and the

distillation was resumed. C was first rinsed out by allowing small portions of the distillate to collect in it and then running it off into

FIG. 1.



B by turning *d*. When about one-third of the chloride had distilled over, *d* was finally closed, and when a sufficient quantity had collected in C the distillation was stopped. The weighed bulbs were now filled by warming and allowing the tetrachloride to pass into them, and each was sealed off in turn at the bend by the blowpipe flame. The detached tubes were carefully cleaned, dried, and weighed with the bulbs belonging to them.

Titanium tetrachloride is violently decomposed by water, and the evolution of heat is so great that a considerable proportion of the dioxide is precipitated as the so-called metatitanic acid. If the solution be not too dilute, and especially if nitric acid be present, the metatitanic acid will gradually dissolve, and eventually the liquid becomes perfectly clear. If solution of silver nitrate be now added, the precipitate of silver chloride which is formed is free from coprecipitated titanic oxide, provided the nitric acid be present in sufficient excess. The rehydration of the titanic oxide and its subsequent solution require some time. A bulb containing 5.6023 grams of pure titanium tetrachloride broken in 35 c.c. of cold distilled water, gave a solution

of about the opacity of milk, which, with occasional shaking, became perfectly clear in about 40 hours. The liquid remained clear, even when heated to about 80° ; at 87° it was milky, and at about 90° or 91° the greater part of the titanous oxide was precipitated. When mixed with an equal bulk of water, the solution was only slightly turbid at 85° , and required to be heated to 95° or 96° before the oxide was precipitated. The effect of the addition of nitric or hydrochloric acid in retaining the hydrate in solution is very marked. Thus, when an equal bulk of strong hydrochloric acid was added to the solution, no precipitate was noticed until at about 98° , and even then it was very faint; on heating to about the boiling point (109°), the turbidity was only very slightly increased.

Titanous acid is known to be soluble in solution of tartaric acid. I found, however, that nothing was gained by decomposing the tetrachloride in solutions of this acid, or by adding the acid to the turbid liquid resulting from the action of water. Indeed the tartaric acid seemed to retard rather than accelerate the solution of the oxide.

If a bulb containing titanium tetrachloride be broken under solution of silver nitrate containing free nitric acid, the precipitated silver chloride is found after a few days to be perfectly free from titanous oxide.

These facts are of importance as tending to simplify the method of analysing the chloride. The clarification of the turbid liquid by standing, and the fact that the precipitated silver chloride is free from titanous oxide, altogether obviate the necessity of removing the titanous oxide previous to the addition of the silver nitrate solution. This is the more fortunate, since titanous hydrate precipitated by ammonia is filtered and washed only with some difficulty and patience.

Series I. $\text{TiCl}_4 : 4\text{Ag}$.

The method of determination in this series was as follows:—The bulb containing the known quantity of the tetrachloride was placed in a well-stoppered bottle together with about 150 c.c. of pure water; the stopper was then firmly tied down, a small wedge being inserted under the string to tighten the fastening, and by a smart jerk the bulb was broken against the side of the bottle. The reaction is very violent, but if care be taken in selecting the bottle and in fastening down the stopper, the decomposition may be safely effected. The turbid liquid was set aside for a few days to clarify. In the meantime, a quantity of the silver slightly less in amount than would be required to combine with the chlorine—on the assumption that the atomic weight of titanium is 50—was weighed out, placed in a litre bottle, also fitted with a well-ground stopper, and dissolved at a gentle

heat, and as slowly as possible, in a slight excess of nitric acid of sp. gr. 1·21, the stopper being from time to time lifted so as to allow of the escape of the nitrous fumes. The solution of the silver nitrate was then heated to expel the dissolved gas, which was driven from the bottle by a gentle current of washed air, a quantity of distilled water was added, and thereafter the clear solution of the tetrachloride. The fragments of glass in the small bottle were repeatedly washed by decantation, and the liquid, after standing, added to the main bulk of the solution. The glass was then dried and weighed as a check on the determination of its weight in the first instance. The differences thus found were very small; in no case would they have affected the result in the second place of decimals. The admixture of the solutions of the tetrachloride and silver nitrate was made in a room illuminated by yellow or orange light. The turbid liquid was then briskly shaken until it became clear, and successive small portions of a solution of silver nitrate containing 0·001072 gram silver per cubic centimetre were added until no further turbidity could be perceived. The operation was carried out in substantially the same manner as that described by Stas, the bottles being placed in black cloth bags during the time occupied by the subsidence of the silver chloride.

Table I contains the results thus obtained :—

TABLE I.

Wt. of TiCl_4 (corrected).	Wt. of silver weighed out.	Wt. of silver added from burette.	Total silver employed.	Ratio of Ti : H. H = 1.
2·43275	5·49288	0·03509	5·52797	48·06
5·42332	12·30669	0·01591	12·32260	48·07
3·59601	8·15960	0·01501	8·17461	47·98
3·31222	7·44102	0·08619	7·52721	48·04
4·20093	9·52445	0·02234	9·54679	48·04
5·68888	12·90603	0·02083	12·92686	48·06
5·65346	12·83142	0·02348	12·85490	47·94
4·08247	9·25578	0·02727	9·28305	47·93

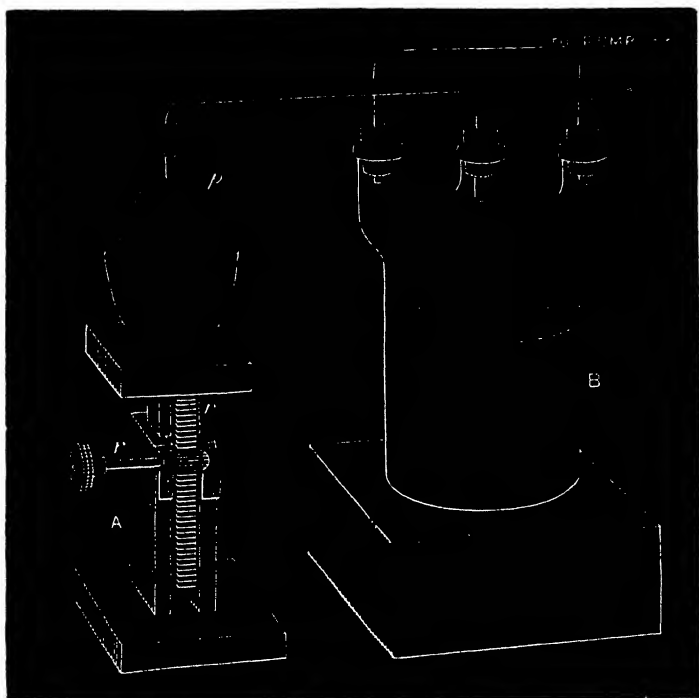
Series II. $\text{TiCl}_4 : 4\text{AgCl}$.

As a further check, and with a view of obtaining an additional value for Ti from the ratio of TiCl_4 to AgCl , the precipitated silver chloride was collected and weighed.

Two porcelain crucibles of 70 c.c. capacity were weighed one against the other by the method of vibrations; one of these was to contain the silver chloride, the other served as a tare. In order to collect the chloride the method of "reverse filtration" was employed. The silver chloride was transferred to the weighed crucible by decan-

tation, the solution of titanic oxide and the washing-water being removed by aspiration through a small disc of filter-paper about 13 mm. radius placed upon the perforated base of a platinum "rose," disc and "rose" being previously weighed with the crucible. The arrangement is seen in Fig. 2.

FIG. 2.



A is a small elevating table, the top of which can be raised or lowered by the rack and pinion, *rr*, so that the "rose," *p*, with the adhering paper disc, may be placed at any required depth within the crucible or withdrawn entirely from it. The "rose" is attached by a piece of narrow flexible rubber tubing to a glass tube leading to the three-necked bottle B. The "rose" can when necessary be placed at right angles to the position shown by hanging it, without detaching it from the rubber tube, upon a glass hook on the tube above. The diminution of pressure within B is effected by the action of a water-jet pump. At *c* is a glass stopcock; by turning it the air can be permitted to flow into B and the aspirating action of the pump immediately arrested. The method of using the arrangement requires but

little explanation. The small disc of paper, which should be cut with a sharp pair of scissors so as to leave a clean edge, is placed against the "rose," moistened with water, and accurately adjusted, so that the periphery of the paper is concentric with the rim of the "rose." The cock *c* is closed, and the water-pump set in action so as to draw up the paper against the face of the platinum "rose." The crucible is then nearly filled with the clear solution of the titanic oxide, and without stopping the action of the pump the "rose" and paper are immersed in the liquid, which is drawn over into B, the crucible being replenished from time to time with fresh portions of the solution. The chloride, from which the solution is drained off as far as possible, is then treated with successive small quantities of dilute nitric acid, thoroughly washed with water, and transferred to the crucible. The liquid in the crucible may be drawn off until the chloride is almost dry. The "rose" with its adhering paper is then detached from the tube, allowed to fall on the cake of the chloride, and the whole is dried in the steam-bath, when the crucible is transferred to the air-bath and heated for some hours at about 160° until its weight is constant. Direct experiment has shown that silver chloride can be thoroughly dried at this temperature if heated for a sufficient length of time. On no occasion, after the weight had become constant, did the chloride suffer a diminution of weight by fusion that would affect the second decimal place in the result; usually the difference was almost inappreciable.

The method of reverse filtration was originally devised by Professor Carmichael, of Bowdoin College (*Zeits. f. Chemie*, N.F., 6, 481; *Fres. Zeits.*, 10, 82), but the arrangement of the apparatus used by me is practically the same as that described by Professor J. P. Cooke (*Proc. Amer. Acad. Arts and Sciences*, 12, 124), and employed by him in his determination of the atomic weight of antimony (*loc. cit.*, 13, 1).

The results obtained by weighing the silver chloride are seen in Table II.

TABLE II.

Wt. of TiCl_4 (corrected).	Wt. of AgCl (corrected).	Ratio Ti : H. H = 1.
3.31222	10.00235	47.99
4.20093	12.68762	47.97
5.68888	17.17842	48.00
5.65346	17.06703	48.05
4.08247	12.32442	48.05

The weighed chloride was then digested with ammonia in order to ascertain its freedom from coprecipitated titanic oxide: in no in-

stance was this detected. The most stringent evidence of the absence of this substance is, however, afforded by a comparison of the amount of the silver chloride found with the known weight of the silver used in the first series. The total weight of the silver chloride obtained was 69·25983 grams : it was formed from 52·13881 grams of silver.

Now $52\cdot13881 : 69\cdot25983 = \text{Ag} : \text{AgCl} = 1 : 1\cdot3284$.

Stas found from seven experiments in which, in the aggregate, 969·3548 grams of silver were found to give 1287·7420 grams of silver chloride, that—

$\text{Ag} : \text{AgCl} = 1 : 1\cdot32845$.

The two ratios, it will be seen, are almost identical.

Series III. $\text{TiCl}_4 : \text{TiO}_2$.

In these experiments the weighed portions of the tetrachloride contained in glass bulbs were decomposed by water in well-stoppered bottles and the solution decanted into a weighed platinum dish of 60 c.c. capacity. The dish was supported on a glass rim over the water-bath, and during the evaporation of the titanic oxide solution it was covered with a large glass shade exactly as in the process of evaporation in Frankland's method of water analysis. When the residue was nearly dry, the dish was filled up with a dilute solution of ammonia, a similar amount of ammonia solution, together with the same quantity of distilled water which had been used in decomposing the tetrachloride and decanting the solution, being evaporated down in the tare. The addition of ammonia to the dried titanic oxide was found to be absolutely necessary to complete the decomposition of the chloride; when the strong hydrochloric acid solution of the oxide is evaporated to dryness and heated, a notable quantity of titanium escapes either as oxychloride or tetrachloride, and a portion is found to have sublimed on the platinum covering of the crucible. No such sublimate is formed after the addition of ammonia.

Titanic oxide is too hygroscopic to be weighed in the ordinary way with free exposure to air. Even after prolonged and intense heating, whereby it shrinks very considerably in bulk and becomes granular, it still absorbs appreciable quantities of moisture if freely exposed to the air. In weighing it, therefore, the crucible containing the titanic oxide was placed under a cover made by inverting a light glass crystallising dish on a thin piece of polished plate-glass; between the plate and the dish was a narrow circular strip of thin sheet caoutchouc, against which the dish was pressed by an india-rubber band. The cover thus made fitted perfectly air-tight, and the

titanic oxide might be allowed to stand for hours on the pan of the balance without any perceptible increase of weight. In order to guard against any change of weight arising from oxidation of the rubber or from its hygroscopic nature, the cover was weighed immediately before and immediately after the determination of the weight of the titanic oxide.

Table III contains the results.

TABLE III.

Wt. of TiCl_4 (corrected).	Wt. of TiO_2 (corrected).	Ratio Ti : H. H = 1.
6.23398	2.62825	47.93
8.96938	3.78355	48.00
10.19853	4.30128	47.99
6.56894	2.77011	47.96
8.99931	3.79575	47.98
8.32885	3.51158	47.94

TITANIUM TETRABROMIDE.

This compound was first prepared by Mr. Francis B. Duppa, who obtained it by passing bromine vapour over a strongly heated mixture of titanic oxide and charcoal (*Proc. Roy. Soc.*, 8, 42). I find that it can be readily prepared by the action of hydrobromic acid gas upon the tetrachloride.

About 350 grams of titanium tetrachloride were placed in a distilling flask connected with an upward condenser and heated to a few degrees below its boiling point, and a steady stream of hydrobromic acid gas, produced by the action of bromine upon a mixture of amorphous phosphorus and water, was led into it. The hydrobromic acid gas was freed from vapour of bromine by passing through a U-tube filled with fragments of glass and amorphous phosphorus, and was dried by passing through a second U-tube containing calcium chloride. To ensure the complete displacement of the chlorine in the tetrachloride, the passage of the hydrobromic acid was continued for about three days. As the subsequent analyses will show, the product was perfectly free from chlorine.

With respect to the physical properties of titanium tetrabromide, I have but little to add to the description already given by Mr. Duppa. It is a beautifully crystalline substance of a dark-yellow or orange colour, melting at about 40° , and boiling at 229° (uncorr.). It is very hygroscopic, and is readily decomposed by water with the evolution of comparatively little heat and with the production of a perfectly clear solution.

To collect it for the purpose of analysis, an arrangement very similar to that used in the case of the chloride was employed. About 400 grams of the recently distilled tetrabromide were placed in a distilling flask connected with a short wide tube leading to the vessel (Fig. 1), in the upper neck of which were placed a number of thin glass bulbs, previously weighed, and identified by means of attached labels of thin sheet zinc, marked with the number of the bulbs. (The labels were not weighed with the bulbs.) About one-third of the tetrabromide was then distilled over into C, and allowed to flow into the bottle. If the bromide showed any signs of solidification it could be readily melted by gently warming the vessel C. Another third portion of the tetrabromide was then distilled over and strongly heated when in C, so as to prevent any chance of its solidifying in the capillary tubes of the bulbs. These were then heated and filled in exactly the same manner as in the case of the chloride.

Series IV. $\text{TiBr}_4 : 4\text{Ag}$.

Weighed portions of the tetrabromide were decomposed by water, and the clear solution treated in precisely the same manner as in Series I. As no metatitanic acid was formed, the liquid could be immediately mixed with the solution of the known weight of the silver.

The addition of the silver solution was made in a room illuminated by yellow light, and the determination of the point of final precipitation effected as described on p. 122.

The results are contained in Table IV.

TABLE IV.

Wt. of TiBr_4 (corrected).	Wt. of silver weighed out.	Wt. of silver added from burette.	Total silver employed.	Ratio of Ti : H. H=1.
2.854735	3.33148	0.01779	3.34927	48.04
3.120848	3.64302	0.01820	3.66122	48.06
4.731118	5.52498	0.02589	5.55097	48.02
6.969075	8.16733	0.00912	8.17645	48.03
6.678099	7.82424	0.01069	7.83493	48.04

Series V. $\text{TiBr}_4 : 4\text{AgBr}$.

The precipitated silver bromide was filtered off in the manner described in Series II (p. 122), dried at 160° , and weighed. The results are seen in Table V.

TABLE V.

Wt. of TiBr_4 (corrected).	Wt. of AgBr (corrected).	Ratio of $\text{Ti} : \text{H}$. $\text{H} = 1$.
3.120848	6.375391	47.95
4.731118	9.668901	47.99
6.969075	14.227716	48.19
6.678099	13.639956	48.02

The total amount of the silver bromide obtained in Series V was 43.90694 grams: it was formed from 25.22357 grams of metallic silver employed in the preceding series.

Now $25.22357 : 43.90694 = \text{Ag} : \text{AgBr} = 1 : 1.7407$.

Marignac (*Bibl. Univ. Genève*, 46, 360) found from three experiments in which, in the aggregate, 60.120 grams of silver afforded 104.648 grams of silver bromide, that—

$\text{Ag} : \text{AgBr} = 1 : 1.74077$.

Stas (*Nouv. Rech.*, p. 158, 1865) obtained in five experiments 459.1681 grams of silver bromide from 263.7669 grams of silver. Hence—

$\text{Ag} : \text{AgBr} = 1 : 1.74081$.

The ratio deduced from my experiments agrees satisfactorily with that resulting from the observations of Stas and Marignac.

Series VI. $\text{TiBr}_4 : \text{TiO}_2$.

The weighed portions of the tetrabromide contained in bulbs were broken under water as in Series III, and the liquid evaporated to dryness, the residue treated with ammonia solution, and strongly heated. It was found impossible to make use of platinum dishes, as these were attacked by the free bromine evolved from the concentrated solution of hydrobromic acid. The evaporation was accordingly made in large porcelain crucibles, a quantity of water and ammonia equal to the amounts employed in the decomposition of the bromide being evaporated in a precisely similar crucible used as a tare, and both crucibles were heated side by side in the same muffle, and otherwise treated in exactly the same way. The results of three experiments are seen in Table VI.

TABLE VI.

Wt. of TiBr_4 (corrected).	Wt. of TiO_2 (corrected).	Ratio of $\text{Ti} : \text{H}$. $\text{H} = 1$.
6.969730	1.518722	48.08
8.836783	1.923609	47.97
9.096309	1.979513	47.94

All the experiments which were made either for the estimation of the bromine or chlorine, or for that of the titanic oxide yielded by the decomposition of the tetrabromide or tetrachloride, are given with the exception of four; one of these was made upon a small quantity of material and was considered as preliminary; the other three mis-carried.

Calculation of the Results.

In order to enable an opinion to be formed as to the agreement among the several observations, the value of Ti has been calculated from each experiment. But probably the most accurate values of the atomic weight are to be deduced from the aggregate weights of the tetrachloride, silver, silver chloride, and titanic oxide; and of the tetrabromide, silver, silver bromide, and titanic oxide, respectively. It is to be presumed that the employment of large quantities of material tends to increase the accuracy of the results; hence the influence of the larger quantities is directly felt by calculating the final values from the aggregate weights in the several series instead of merely taking the means of the several observations.

I assume with Lothar Meyer and Seubert that the most probable ratios of Ag, Cl, Br, O, and H are as follows:—

$$\begin{aligned}\text{Ag} &= 6\cdot7456 \\ \text{Cl} &= 2\cdot21586 \\ \text{Br} &= 4\cdot99721 \\ \text{O} &= 1 \\ \text{H} &= 0\cdot06265.\end{aligned}$$

Adopting these numbers, we may thus summarise the results of the various observations:—

Series I (8 experiments).

$$\begin{aligned}\text{TiCl}_4 : 4\text{Ag} &= 34\cdot39004 : 78\cdot16399 \\ &= 1\cdot75989 : 4 \\ \text{TiCl}_4 : \text{O} &= 11\cdot8715 : 1 \\ \text{Ti} : \text{O} &= 3\cdot0081 : 1 \\ \text{Ti} : \text{H} &= 48\cdot014 : 1\end{aligned}$$

Series II (5 experiments).

$$\begin{aligned}\text{TiCl}_4 : 4\text{AgCl} &= 22\cdot93796 : 69\cdot25983 \\ &= 1\cdot32475 : 4 \\ \text{TiCl}_4 : \text{O} &= 11\cdot8716 : 1 \\ \text{Ti} : \text{O} &= 3\cdot0082 : 1 \\ \text{Ti} : \text{H} &= 48\cdot016 : 1\end{aligned}$$

Series III (6 experiments).

TiCl ₄ : TiO ₂	=	49·29948	:	20·79032
	=	2·37124	:	1
Ti : O	=	3·0053	:	1
Ti : H	=	47·969	:	1

Series IV (5 experiments).

TiBr ₄ : 4Ag	=	24·35387	:	28·57284
	=	3·40937	:	4
TiBr ₄ : O	=	22·99827	:	1
Ti : O	=	3·0094	:	1
Ti : H	=	48·031	:	1

Series V (4 experiments).

TiBr ₄ : 4AgBr	=	21·49914	:	43·90696
	=	1·95861	:	4
TiBr ₄ : O	=	22·99960	:	1
Ti : O	=	3·0107	:	1
Ti : H	=	48·057	:	1

Seriés VI (3 experiments).

TiBr ₄ : TiO ₂	=	24·90283	:	5·42184
	=	4·59311	:	1
Ti : O	=	3·0065	:	1
Ti : H	=	47·989	:	1

It is of course possible that these various values do not merit the same degree of confidence, but I am unable on any precise *à priori* grounds to apportion the relative weights which should be attributed to them in taking a final mean. Each set of determinations has its special difficulties, and is liable to errors of which we have no method of assessing the numerical value. Titanium tetrachloride is very susceptible to change in contact with moisture, and is generally more difficult to work with than the bromide, and, as is well known, the end-point in the precipitation by Gay-Lussac's method cannot be so precisely hit in the case of chlorides as in that of bromides. Series II and V may be affected by the relative solubilities of the silver salts. On the other hand, the tetrabromide is rather more difficult of preparation in a pure state than the chloride. At first sight, the determinations of the oxide, yielded by the decomposition of the two bodies, might be deemed to afford the most trustworthy basis, as the method employed is the simplest in principle; but titanous oxide is extremely difficult to dehydrate, and rehydrates itself with rapidity in contact with moist air. Indeed, titanous oxide would form an

excellent medium for the study of molecular absorption in the manner indicated by van Bemmelen (*J. pr. Chem.* [2], 26, 227).

On the assumption, therefore, that these values have equal weights, the final value from the whole 31 experiments becomes—

$$\text{Ti} = 48.013.$$

			Diff. from mean.
Series	I.....	48.014	+ 0.001
	II.....	48.016	+ 0.003
	III.....	47.969	— 0.044
	IV.....	48.031	+ 0.018
	V.....	48.057	+ 0.044
	VI.....	47.989	— 0.024
	Mean	48.013	

Probable error of one series = \pm 0.021

Probable error of result .. = \pm 0.0085

This number, 48.01, differs but slightly from that obtained by Rose in the experiments on which he set the greatest weight; it varies, however, by more than two units from the final number adopted by Pierre, viz., 50.25, and which has hitherto been commonly accepted as the most trustworthy value for Ti.

It will be observed, too, that the number 48.01 is in accordance with the value required by the Periodic Law. Mendeleeff's prevision thus receives a complete experimental confirmation.

It will also not escape notice that 48.01 is practically a whole number. It might be urged that the remarks made by Mallet at the close of his admirable memoir on the atomic weight of aluminium (*Phil. Trans.*, 171, 1033) are hardly less applicable to the case of titanium. We must, I think, concede, with Mallet, that facts impartially looked at require us to admit that Prout's hypothesis is not as yet absolutely overthrown. Even if we discard altogether Dumas' assumption, and have regard only to the indications of Prout's law, in the form originally enunciated by him, the fact that so large a proportion of the very best determined values approximate to integers is too significant to be lightly set aside. Nevertheless, I do not wish to attach an undue importance to the instance of titanium. Anyone who has worked at all with the haloid compounds of this element would, I think, refrain from basing a conclusion of so momentous a character on the unsupported evidence which such bodies might afford. I should suppose that these substances would be among the very last compounds which any chemist who set himself to test the validity of Prout's law would select as affording a suitable experimental basis.

I desire, in conclusion, to express my acknowledgments to the Society for their very liberal grant from the Research Fund towards the expenses of this investigation. My thanks also are due to my assistant, Mr. Herbert Ingle, for his ready and intelligent aid in what has proved to be a somewhat tedious and protracted piece of work.

XVI.—*Note on the Constitution of Propylene Chlorhydrin.*

By Dr. H. FORSTER MORLEY and ARTHUR G. GREEN, Tufnell Scholar at University College.

PROPYLENE chlorhydrin, from whatever source it may have been obtained, is always found to boil at 127—128°, although two isomers are indicated by theory.

According to Markownikoff (*Annalen*, 153, 254), the chlorhydrin, prepared by the union of propylene with hypochlorous acid, is converted into chloracetone by oxidation with potassic dichromate and sulphuric acid. His statement, however, is not supported by analytical data.

The same chlorhydrin was subsequently examined by Henry (*Compt. rend.*, 79, 1258), who found that it was oxidised to chloropropionic acid by treatment with nitric acid.

From this result he concluded that the chlorhydrin was primary $\text{CH}_3\text{.CHCl.CH}_2\text{.OH}$, and suggested that Markownikoff might have mistaken chloropropionic aldehyde for chloracetone; he admits, however, that the chlorhydrin obtained by Oppenheim's method (*Annalen*, Suppl. vi, 367), from allyl chloride (by hydration), has the formula $\text{CH}_3\text{.CH(OH).CH}_2\text{Cl}$, because anhydrous phosphoric acid reconverts it into allyl chloride. Since it is now possible to obtain considerable quantities of propylene chlorhydrin from glycerol, we have examined the product obtained from this source.

Preparation of Propylene Glycol.

550 grams of coarsely powdered caustic soda are heated with 1300 grams of commercial glycerol (about 95 per cent.), in an iron retort (5 litres capacity), until the glycerol has dissolved as much soda as it can take up without decomposition, the retort is then closed, and the contents carefully distilled. From the aqueous portion of the distillate, 140 grams of propylene glycol (boiling at 185—195°)

can be obtained by fractional distillation. Above 190° , a further fraction (27 grams) is obtained, probably containing trimethylene glycol.

Propylene Chlorhydrin.

250 grams of propylene glycol are shaken with 500 grams of chloride of sulphur, and the evolution of hydric chloride, which begins in the cold, is completed by heating the mixture for five or six hours on the water-bath. The liquid is then decanted and, after the addition of the ethereal extract of the residual sulphur, is shaken with a saturated solution of potassic carbonate, dried over solid potassic carbonate, and distilled. In this way, 170 grams of propylene chlorhydrin may be obtained, boiling at $127-128^{\circ}$, and free from sulphur compounds.

Oxidation of Propylene Chlorhydrin.

We have employed for this purpose, (a) potassic dichromate and sulphuric acid, (b) chromic acid and dilute sulphuric acid, (c) chromic acid and glacial acetic acid, (d) strong nitric acid, but find that chloracetone is invariably produced.

As an example, 60 grams of sulphuric acid were mixed with 40 grams of water and slowly added to a solution of 40 grams of chlorhydrin and 44 grams of potassic dichromate in 160 c.c. of water. A pungent oil rose to the surface, and was found to be a mixture of chloracetone with undecomposed chlorhydrin. The chloracetone was recognised by the characteristic crimson colour which it gives with a saturated solution of potash, and its presence proved by reduction to acetone. For this purpose, zinc and hydrochloric acid were used, and the bisulphite compound obtained from the acetone so produced, was analysed:

0.22 gram gave 0.099 gram Na_2SO_4 .

	Calculated.	Found.
Na.	14.2	14.57

Hence the propylene chlorhydrin consists, at any rate for the most part, of $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{Cl}$. On oxidation, the primary chlorhydrin should give chloropropionic acid or its aldehyde, and we are led to think that a small quantity of an aldehyde is contained in the product of oxidation; for, even after the complete reduction of the chloracetone to acetone, the liquid is still capable of readily forming a silver mirror, of reddening a solution of rosaniline that has been decolorised by sulphurous acid, and of producing an odour of aldehyde resin when warmed with potash. We are therefore by no means

certain that the secondary chlorhydrin is not mixed with the isomeric compound $\text{CH}_3\text{CHCl.CH}_2\text{OH}$.

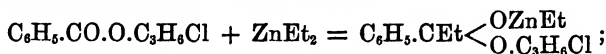
In order to obtain further evidence of its constitution, we tried to reduce the chlorhydrin to a propyl alcohol, but were unable to effect this in acid solutions, whilst in alkaline solutions the formation of propylene oxide (which would reduce to isopropyl alcohol) is not excluded. These remarks apply also to its benzoate and acetate (b.p. 151° corr.).

XVII.—*Action of Zinc Ethide on the Benzoate of Propylene Chlorhydrin.*

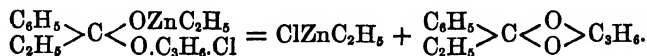
By Dr. H. FORSTER MORLEY, M.A., and ARTHUR G. GREEN,
Tufnell Scholar at University College.

IN order to obtain additional evidence of the correctness of our view as to the constitution of propylene chlorhydrin, we attempted to prepare an amyl compound from it by the action of zinc ethide. But since Butlerow (*Annalen*, 144, 43) states that ethylene chlorhydrin is not converted into butyl alcohol by zinc ethide, whilst an isomeric change occurs in the formation of this alcohol from ethylene iodhydrin, we selected the benzoyl derivative of the chlorhydrin for our experiments.

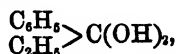
We find, however, that instead of attacking the chlorine, the zinc ethide attaches itself to the carbonyl-group



and that afterwards zinc chlorethide is eliminated :



This agrees with the experiments of Wagner and Saytzeff (*Annalen*, 175, 361) on the synthesis of tertiary butyl alcohol from acetyl chloride. Our compound may be viewed as the propylene ether of an ethyl phenyl orthoketone :



and has the same relation to ethyl phenyl ketone that acetal has to aldehyde. It might be called propylene ethyl phenyl orthoketone, but

since the use of the term "ortho" in an aromatic compound in this sense is undesirable, we propose to name the compound propylene ethylphenylketate, the term ketate being derived from ketone (*sci.*, orthoketone), somewhat as alcoholate has been derived from alcohol.

Chlorisopropyl Benzoate, $C_6H_5.CO.O.C_3H_7Cl$.

118 grams of benzoyl chloride are heated with 80 grams of propylene chlorhydrin for one hour on the water-bath, and afterwards on an oil-bath at 170° , until no more hydrogen chloride comes off. The product is washed with water, dried over calcic chloride, and distilled. The yield is quantitative. Analysed by the method of Plimpton and Graves—

- I. 0.2952 gram substance gave 0.22 gram $AgCl$.
 II. 0.3500 " " " 0.2585 gram $AgCl$.

	I.	II.	Calculated.
Cl	18.44	18.27	17.88

The benzoate of propylene chlorhydrin is insoluble in water, has very little odour, and is saponified by alkalis with extreme ease, producing propylene oxide.

Its sp. gr. is 1.172 at 19° , and 1.149 at 45° .

Propylene Ethylphenylketate.

60 grams of zinc ethide are dissolved in 100 grams of toluene and heated to boiling; 80 grams of chlorisopropyl benzoate are then run in slowly. The reaction takes place quietly, and after two or three hours it is complete; on cooling, a solid mass usually separates. The entire product is then treated with water, and the separated zinc hydroxide brought into solution by the addition of sulphuric acid; the layer of toluene is heated with aqueous potash, dried over solid potash, and fractionated. The product comes over between 210° and 230° in air, and 110 — 120° in a vacuum. The yield is satisfactory. Analyses of various portions gave the following results:—

- I. 0.339 gram substance produced 0.9426 gram CO_2 and 0.26 gram H_2O .
 II. 0.2584 gram substance produced 0.7255 gram CO_2 and 0.1992 gram H_2O ,

whence the following numbers are calculated:—

	I.	II.	Calculated for $C_{12}H_{16}O_2$.
C	75.84	76.56	75.0
H	8.52	8.57	8.33

Although the carbon is more than 1 per cent. too high, yet the numbers agree better with our formula than with any other that could reasonably be suggested. The high numbers are due to an impurity (possibly a hydrocarbon) which remains undissolved on mixing the compound with strong sulphuric acid. Unfortunately, we have hitherto been unsuccessful in our attempts to remove this impurity; but we hope, by modifying the method of preparing the ketate, to avoid its production. The ketate is a colourless liquid, insoluble in water; it boils undecomposed at about 235° (corr.), and its sp. gr. at 22° is 0.99. It has a pleasant odour. Although it is isomeric with amylic benzoate, the body we expected to be formed, it is not saponified even by heating with alcoholic potash at 170° . It does not contain hydroxyl, since acetyl chloride does not act on it. Sodium may be melted under it without evolution of hydrogen. It does not form compounds with hydroxylamine or phenylhydrazine, so that it is not a ketone. It is not affected by heating to 115° with strong hydrochloric acid. It reacts readily with bromine, producing a pungent, monobrominated derivative, which boils, with partial decomposition, at about 230° . Both the ketate and its bromo-derivative are volatile with steam.

Oxidation of the Ketate.

10 grams of the ketate were boiled with 60 grams of nitric acid (sp. gr. 1.4), diluted with 20 c.c. of water, until the oil was dissolved. On cooling, a mass of crystals of benzoic acid separated, weighing about 6 grams. In order to see whether any homologue of benzoic acid was present, the crystals were fractionally distilled with steam, and the crystals which separated from the successive distillates, as well as those which could be obtained from their mother-liquors, were examined. Nothing but benzoic acid, melting at 122° , could be found. The nitric acid solution, from which the benzoic acid had separated, was neutralised by ammonia and distilled, after the addition of ferric chloride. The distillate, which contained formic acid, was neutralised with soda, evaporated to dryness, mixed with concentrated sulphuric acid, and redistilled. The distillate was recognised as acetic acid, and its silver salt was analysed.

0.1956 gram substance gave 0.1257 gram silver.

	Found.	Calculated.
Ag.	64.26	64.67

Lactic acid was looked for, but not found.

The ketate, therefore, gives benzoic acid and acetic acid on oxidation.

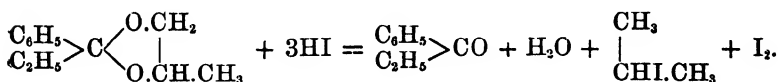
Action of Hydriodic Acid.

Below 150°, hydriodic acid has little action on the ketate.

15 grams of the ketate were heated for six hours at 200° with 60 grams of hydriodic acid (50 per cent. solution) and about 1 gram of red phosphorus. No gas escaped on opening the tube, but a quantity of iodine separated. The oily layer was shaken with dilute potash, and distilled with steam. It was then dried over calcic chloride, and fractionated. Two liquids were thus obtained, one boiling at 90°, and the other at 200–220°. The first is isopropyl iodide; the somewhat high percentage of iodine may perhaps be due to a trace of iodoform or of propylene iodide.

	Found.	Calculated for	
		C ₂ H ₅ I.	C ₃ H ₇ I.
I	76.2	81.4	74.7

From the portion boiling between 200° and 220°, phenyl ethyl ketone can be isolated, either by exposure to a freezing mixture, or by the following method:—2½ grams of the oil are heated with 20 c.c. of Fischer's 10 per cent. solution of the hydrochloride of phenylhydrazine. The oily product is separated and distilled with steam, by which means the volatile portion is removed, and the compound of the ketone with phenylhydrazine remains behind. This compound is then decomposed by sulphuric acid, and the regenerated ketone distilled off with steam. After drying with calcic chloride and distilling, the ketone solidifies on cooling to 0°. The crystals were pressed between blotting-paper and found to melt at 21°. The reaction is—

*Action of Sulphuric Acid on the Ketate.*

When equal volumes of the ketate and of sulphuric acid are shaken together, heat is evolved, and the ketate dissolves, leaving its impurity in the form of a viscid oily layer. On pouring the sulphuric acid into water, phenyl ethyl ketone separates as a light oil, which is distilled with steam, dried, and distilled. The entire liquid, boiling between 210° and 220° (uncorr.), solidifies on cooling to a mass of beautiful, thin, crystalline plates, which, after pressure between blotting-paper, melt at 21°, and boil constantly at 218° (corr.). On analysis, 0.2762 gram gave 0.8108 gram CO₂, and 0.1853 gram water.

	Observed.	Calculated for $C_6H_5.CO.C_2H_5$.
C	80.05	80.6
H	7.45	7.46

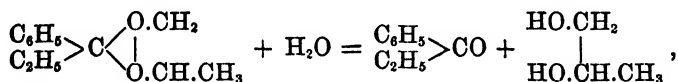
The vapour-density, determined by V. Meyer's method, in β -naphthol vapour, was found to be—

Observed.		Calculated.
I.	II.	
4.52	4.75	4.64

The mean of these determinations gives the molecular weight 134, agreeing with theory. We prepared the nitro-derivative from our ketone, and found, in accordance with Barry's statement (*Ber.*, 6, 1007), that it melted at 100°.*

In order to isolate the other product of the action of sulphuric acid on the ketate, the solution, after removal of the ketone, was neutralised with lime, filtered, and the water removed by distillation out of a long-necked flask. A liquid boiling at 185° is left. This has a sweet taste, is soluble in water, and was recognised as propylene glycol by converting it into propylene oxide by successive treatment with chloride of sulphur and potash.

The action of sulphuric acid on the ketate may therefore be represented thus:—



although it, of course, takes place in two stages.

The monobrominated ketate appears to undergo a similar decomposition producing an intensely pungent oil, probably phenyl α -bromethyl ketone, $C_6H_5.CO.CHBr.CH_3$.

We propose to continue our investigation of this and other allied ketates, and also to examine the behaviour of zinc ethide towards chlorinated compounds containing the carbonyl-group.

* It is a curious fact that all previous observers have described phenyl ethyl ketone as a liquid. We have prepared some by distilling a mixture of calcic benzoate and calcic propionate, and find, as we expected, that it is a solid crystallising in large thin plates which melt at 21°. Its boiling point is 218° (corr.), which is somewhat higher than that usually given.

XVIII.—*The Alkaloids of Nux Vomica.* III. *Some Experiments on Strychnine.*

By W. A. SHENSTONE, Lecturer on Chemistry in Clifton College.

IN 1883 (Trans., p. 101) I read a paper before the Society showing that brucine contains two methoxyl groups, and is probably a dimethoxyl derivative of strychnine, as represented by the formula $C_{21}H_{20}(CH_3O)_2N_2O_2$. I have been unavoidably delayed in the further examination of this question, but am now working upon it in conjunction with Mr. A. Richardson.

Meanwhile, my experimental results have been in some degree confirmed by the work of A. Hanssen (*Ber.*, 17, 2266), who has obtained methyl chloride and a complementary base from brucine by the use of the same reagent that I employed, viz., hydrochloric acid. Apparently Hanssen was unaware of my experiments, and he has not carried the action so far as I did, nor has he noticed its probable bearing on the relationship between the two alkaloids in nux vomica beans. Since this relation between these bodies occurred to me, I have been much interested in the constitution of strychnine, and, amid many interruptions, have lately made the experiments recorded in this paper. Meanwhile several other chemists have also turned their attention to the subject. Thus, Plugge (*Chem. News*, 1883), by oxidising it with potassium permanganate, has obtained an acid, $C_{11}H_{11}NO_3, H_2O$; Hanriot has re-examined nitrostrychnine; Goldschmidt (*Ber.*, 15, 1977) has recognised, qualitatively, indole as a product of the distillation of strychnine with caustic potash; and Scichilone and Magnanimi (*Gazzetta*, 12, 444) believe that by distillation with zinc-dust they have obtained a new isomeride of the known lutidines from strychnine.

At the end of my last paper, I expressed my intention of working on strychnine in future, as I had reason for thinking it would prove more satisfactory than brucine; and at the subsequent suggestion of Dr. Armstrong, who I believe some years ago had a similar object in view, I decided to employ its bromo-derivative, as likely to give better results, and in order that at the same time the physiological action of this compound might be examined. This, as a subsequent paper will show, has been done by Dr. Lauder Brunton.

The halogen compounds of strychnine have been already incompletely investigated, Herapath and Tilden having prepared some iodine compounds, and Laurent those of chlorine and bromine.

Laurent observed that when bromine is added to a strong solution of

strychnine hydrochloride and the resinous precipitate is filtered off, the solution yields to ammonia a precipitate of bromostrychnine, crystallising from spirit and forming a crystalline hydrochloride. As I had reason for thinking that nearly all the alkaloid would be precipitated as resin if this method were followed, I attempted, but without success, to prepare bromostrychnine by adding a solution of bromine in chloroform to solution of strychnine in the same solvent. I found, however, that by adding bromine-water to the hydrochloride dissolved in 50 to 100 times its weight of water, no considerable proportion of resin was formed till two equivalent proportions of bromine had been added. From this solution, alkalis threw down a solid, insoluble in water, and crystallising beautifully from warm alcohol; this evidently corresponded with Laurent's compound. There was no difficulty in completely converting strychnine into this substance.

A portion was crystallised in two fractions. 0.2626 gram of the first fraction gave 0.1188 gram silver bromide, equivalent to 19.23 per cent. of bromine; 0.3070 gram of the second fraction gave 0.1383 gram of AgBr, equivalent to 19.15 of bromine.

Theory for $C_{21}H_{21}BrN_2O_2$ requires 19.37 per cent. bromine.

The platinochloride of this compound is not quite stable; its colour slightly changes during drying. A specimen was examined, however, and was found to contain 17.2 per cent. Pt, as against 16.03 required by the above formula.

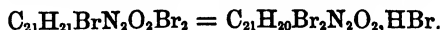
The crystallography of bromostrychnine is given in a separate note by Mr. H. A. Miers appended to this paper.

I found bromostrychnine to be fairly soluble in cold, and more so in hot alcohol; also soluble in chloroform. It unites very readily with methyl iodide, the methiodide separating in crystals when methyl iodide is added to an alcoholic solution of monobromostrychnine. Monobromostrychnine forms a hydrochloride, which, on evaporation, yields gelatinous masses, and these soon set into silky needles.

Having observed that by the addition of four equivalent proportions of bromine to solutions of strychnine practically all the strychnine is thrown down as the resin mentioned by Laurent, I was led to suspect its nature. If precipitated at about 40° , it can be secured easily as a bright yellow powder, which slowly evolves bromine, is insoluble in water and chloroform, but soluble in alcohol. On analysis, 0.1262 gram gave 0.1293 gram of AgBr, equivalent to 43.58 per cent. of Br. It is therefore dibromide of monobromostrychnine, $C_{21}H_{21}BrN_2O_2 \cdot Br_2$ (which requires 41.8 per cent. bromine), a little contaminated with some other more highly brominated substance. This was confirmed: 1. By the fact that the same body is thrown down on adding bromine to solution of bromostrychnine. 2. That by the action of ammonia, it is changed to a white substance, having

all the properties of bromostrychnine. A specimen of bromostrychnine made in this way was found to contain 21.17 per cent. of bromine, theory requiring 19.37. This is what would be expected from the above facts.

Dibromostrychnine.—When the above precipitate is heated with its mother-liquor for some hours, it presently dissolves. This led me to hope that dibromostrychnine was formed by the reaction



Analyses of the products always show great deficiency of bromine, so there is no doubt that oxidation occurs. Neither did I succeed in effecting the above reaction by heating the dry solid, or by exposing it to sunlight. If, however, solution of bromine in chloroform is added cautiously to a solution of strychnine in the same liquid, there is not much precipitation until two equivalents of bromine have been added. After that, it is rapidly precipitated, probably as a dibromide, analogous to that above described. If the addition of bromine is stopped at the right point, and the solution is treated with alkali, it gives, on evaporation, a resin-like residue, rather easily decomposed by heat; this does not appear to be crystalline. Analysis of a specimen showed it to contain 35.3 per cent. of bromine; so probably it is dibromostrychnine with the formula $C_{21}H_{20}Br_2N_2O_2$, which requires 32.5 per cent. Br, contaminated with some more highly brominated product. Although I have not succeeded in its purification, I hope it will prove useful in some future work.

Chlorostrychnine.—Before proceeding to describe my further experiments with bromostrychnine, I may point out that, although I have not made any experiments on chlorostrychnine, yet the above affords an explanation of the discordant results obtained by Laurent and Pelletier.

The former, by a method analogous to that by which he obtained bromostrychnine, prepared a substance which yielded a crystalline sulphate, and was shown by analysis to be chlorostrychnine, $C_{21}H_{21}ClN_2O_2$; whilst Pelletier, by completely precipitating a solution of strychnine with chlorine, obtained a compound which contained 24.57 per cent. of chlorine. From the mode of its formation, and from the fact that the formula for dichloride of monochlorostrychnine requires 24.2 per cent. of chlorine, I think there can be no doubt that Pelletier's compound stands in the same relation to Laurent's that the above described dibromide does to Laurent's monobromostrychnine; so that for the present I have not thought it necessary to examine them, although possibly they may be of value in the future progress of this work.

Action of Nitric Acid on Bromostrychnine.—When this compound is

heated with excess of strong nitric acid for some hours, copious red fumes are evolved, and the bromine appears to be almost entirely expelled. On concentrating and diluting, a resinous precipitate forms, which consists of the nitrated bodies that have been examined with somewhat varying results by Nicholson and Abel, Claus, Hanriot, and others. The amount of this resin represents a very large proportion of the materials used. The liquid separated from this precipitate was found to have a bright yellow colour, and dyed silk. On neutralising it with potassium carbonate and concentrating, a crop of crystals was obtained which resembled potassium picrate in appearance and solubility; they were explosive. After recrystallisation, a portion was examined quantitatively.

0.2386 gram gave 0.0758 gram of K_2SO_4 . This is equivalent to 14.2 per cent. of potassium. The picrate requires 14.6 per cent.

The acid itself was isolated by extraction with ether from an acid solution of the salt. The residue, on evaporation, melted at about 120° ; it is therefore the 1 : 2 : 4 : 6 trinitrophenol.

On repeating the above treatment with strychnine itself, I got a similar result. When I used ordinary strong nitric acid, I secured $6\frac{1}{2}$ per cent. of picrate; so that allowing for the inevitable loss in working on a small scale, probably the amount was not less than 10 per cent.; and as I estimate that at least half the strychnine remained in the form of insoluble nitrostrychnines, this may be regarded as representing perhaps nearly 20 per cent. of the material actually acted on. When fuming nitric acid was employed, the yield was rather greater, for 12 per cent. of potassium salt was secured. It was, however, accompanied by another substance which could not be removed except with considerable loss, so that the exact amount of picrate was uncertain.

It is singular that this formation of trinitrophenol in a reaction that has been so frequently studied, should have been overlooked hitherto. It is of considerable interest, for it appears to indicate, in the first place, that strychnine contains a benzene-ring of carbon-atoms, and secondly, that it may perhaps contain one or more hydroxyl-groups; the latter inference is supported by the behaviour of strychnine under the action of the alkaline oxidising agents used. This, if correct, is important, as there are so few cases among the alkaloids in which the manner in which the oxygen is united is known.

I am continuing my experiments on this subject, and hope to be able to carry on the work without interruption in the future, and also to extend my observations to other alkaloids. .

XIX.—On the Physiological Action of Brucine and Bromostrychnine.

By T. LAUDER BRUNTON, M.D., F.R.S.

THERE has been a considerable difference of opinion regarding the action of brucine, some saying that its action is like that of strychnine but weaker; others that it was a bitter tonic, with little or no convulsive power. The reason of this difference of opinion is, I think, shown by some experiments which I have made with pure brucine, kindly given to me by Mr. Shenstone. From these experiments, it appears that brucine has a convulsant action resembling that of strychnine, but the action is not only weaker in itself, but is so much lessened in the case of mammals by the rapid elimination of the poison, as to give rise to no symptoms when the brucine is taken by the mouth. Its convulsant action is shown very distinctly when the brucine is injected in solution into the abdominal cavity, so that it is rapidly absorbed, and the whole or nearly the whole of the quantity administered is able to act upon the organism, there being no time allowed for its excretion. When it is taken into the stomach, on the other hand, excretion appears to go on *pari passu* with absorption; there is thus no large quantity of brucine at any one time in the blood, and the animal does not suffer. A decigramme of the hydrochloride of brucine dissolved in 3 c.c. of water, and injected into the abdominal cavity of a white rat, began to act almost immediately. The animal cowered and shivered after the injection; in three minutes it was seized with an emprosthotonic convulsion, and died. A similar quantity given to another rat, mixed with suet so that the animal ate it readily, produced no symptoms whatever. The symptoms produced in a rabbit were peculiar. For a number of minutes after the injection, the animal seemed quite unaffected, then all at once it took a sudden run of a few steps, leapt into the air, and fell dead.

The difference between the effect of brucine and strychnine appears rather to be one of degree than of kind, and to be chiefly dependent on the more ready elimination of brucine. Brucine, like strychnine, produces death by convulsions and not by paralysis, but, like curara, which is also a product of a species of strychnos, it is innocuous when taken into the stomach, though fatal when injected under the skin. I have not yet made comparative experiments between the action of brucine and iodide of methylstrychnine, but on comparing the result of my experiments with brucine and those of Fraser and Crum-Brown on iodide of methylstrychnine, it appears that the two have a different action, the brucine causing convulsions,

whilst the iodide of methylstrychnine produces paralysis. This is a curious point, and is well worthy of investigation, inasmuch as it may throw some light on the chemical constitution of the alkaloid. We find apparently a somewhat similar condition in the alkaloids of opium. By the introduction of alcohol radicles into morphine, substances are produced to which the name of *codeïnes* has been given. In some of these, such as codethyline, $C_{17}H_{18}NO_2 \cdot OC_2H_5$, obtained from morphine by the introduction of ethyl, the narcotic action is diminished, whilst according to Von Schroeder, the convulsant action is increased in proportion to the number of atoms of hydrogen substituted by alcoholic radicles. If such be the case, it is remarkable that by the addition of alcohol radicles to codeïne or thebaine, their tetanising action should be altered into a paralysing action, methyl-thebaine producing paralysis, like methylstrychnine.

Bromostrychnine has an action very much like that of strychnine. In the pithed frog it causes clonic convulsions, which, like those of strychnine, may be brought on by a slight touch, jar, or external irritation. Like the convulsions of strychnine they depend on alterations in the function of the spinal cord, and not on any action of the drug on the higher centres in the brain or medulla, as the effects occur when the brain is completely destroyed, or when the head is cut off.

XX.—*Crystallography of Bromostrychnine.*

By H. A. MIERS, M.A.

CRYSTALLINE system. Rhombic.

$$a : b : c = 1.45907 : 1 : 1.19457$$

$$(100) : (110) = 55^\circ 34\frac{1}{2}'. \quad (010) : (011) = 39^\circ 56'. \quad (001) : (101) = 39^\circ 18\frac{1}{2}'.$$



Bromostrychnine.

The forms observed are:—

$$\begin{aligned} a &= \{100\}. \\ m &= \{110\}. \\ o &= \{101\}. \\ n &= \{102\}. \\ y &= \{112\}. \end{aligned} \quad \text{See Figure.}$$

	Calculated.	Observed.
<i>am</i>	—	55° 34 $\frac{1}{2}$ '
<i>ao</i>	—	50 41 $\frac{1}{2}$
<i>an</i>	67° 44'	67 46
<i>ay</i>	70 38	—
<i>yy</i>	38 44	38 37
<i>my</i>	54 5	53 50

The crystals are colourless and transparent; brittle, with a conchoidal fracture, but without observable cleavage.

Almost all are rectangular tables, exhibiting the faces *a* (large), *o*, *m*, and sometimes *n*.

The faces *y* are rare.

The large faces *a* are marked by curved striations in the direction of the edge *ao*.

XXI.—Formation of Pyridine Derivatives from Malic Acid.

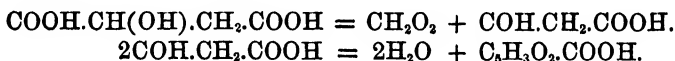
By H. O. PECHMANN and W. WELSH.

THE nature of the chemical changes which take place in the vegetable organism and lead to the absorption of nitrogen is still unexplained; and although there can be no doubt that the nitrogen enters the plant in the form of ammonia and nitric acid, we are unable to follow the steps by which nitrogenous compounds, especially the alkaloids and albuminoids, are elaborated.

The study of the alkaloids has led, as first suggested by Kœnigs (*Studien über die Alkaloide*, München, 1880), to their being regarded as derivatives of pyridine; for although no alkaloid has been artificially prepared hitherto, numerous methods are already known for the synthesis of compounds which must be regarded as pyridine derivatives, and which stand in close relation to the natural alkaloids. Assuming that pyridine compounds are formed in plants, we may endeavour to ascertain what is the nature of the reactions which take place in these natural syntheses.

If, in the formation of alkaloids, it is taken for granted that nitrogen is supplied in the form of ammonia and amido-compounds, non-nitrogenous carbon compounds must also take part in the reaction. Such processes, however, can only be explained if we know substances which, under the ordinary conditions of pressure and temperature, unite with the above-named nitrogen compounds to form pyridine derivatives. As already remarked by V. Meyer and E. Schulze (*Ber.*, 1884, 1554), no such substances have hitherto been known, but we have now, in *coumalinic acid*, which is very easily formed from malic acid, a body which (in its ethereal salts) fulfils the required conditions.

As one of us has recently shown (*Ber.*, 1884, 936), malic acid when acted on by concentrated sulphuric acid, is split up into formic acid and the half-aldehyde of malonic acid; 2 mols. of the latter in the nascent state then undergo condensation with elimination of the elements of 2 mols. of water, and form coumalinic acid, $C_6H_5O_2.COOH$; this is shown by the equation—

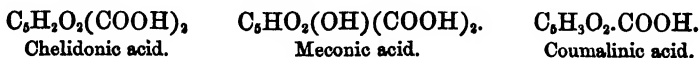


Coumalinic acid at once enters into reaction with ammonia even at the ordinary temperature, forming hydroxynicotinic acid. Thus:—



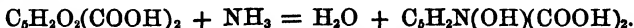
Primary amines and amido-acids behave similarly with coumalinic acid, reacting with it to form hydroxypyridinecarboxylic acids. The production from malic acid of derivatives of nicotinic acid, which, as is well known, stands in close relation to numerous alkaloids, is of especial interest, in so far as similar changes probably take place in plants.

The occurrence of chelidonic acid and meconic acid in certain Papaveraceæ is well known, and although the constitution of these compounds is not yet ascertained, important indications of their true nature have been obtained. A comparison of their composition and properties discloses analogies between these vegetable acids and coumalinic acid. They may all be regarded as derivatives of a group of the empirical formula $C_6H_4O_2$, although the constitution of this group does not appear to be invariable. Thus:—

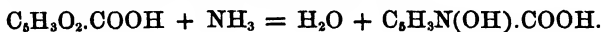


Chelidonic and meconic acids form two series of salts, of which one series is colourless, the other yellow; coumalinic acid also possesses this property. Chelidonic acid and members of the meconic

acid group, as has been specially established in the case of coumalic acid, are decomposed when boiled with alkalis or alkaline earths, acetone being one of the products. Under like conditions, coumalinic acid yields a compound having the character of an aldehyde and probably identical with crotonaldehyde. Finally, in their peculiar behaviour with ammonia, these acids exhibit the greatest resemblance, being converted into hydroxypyridinecarboxylic acids. Chelidonic acid, for example, reacts with ammonia to form hydroxypyridinecarboxylic acid—



This reaction corresponds with that of the conversion of coumalinic acid into hydroxypyridinemonocarboxylic acid—

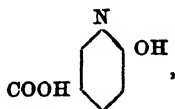


It is to be noted that in the case of coumalinic acid this reaction takes place at the ordinary temperature; whereas, in the case of the other acids, heat or increased pressure is necessary.

Bearing in mind, then, that chelidonic and meconic acids are invariably accompanied in the plants in which they occur, not only by malic acid, citric acid, and similar simple vegetable acids, but also by alkaloids; moreover, that chelidonic and meconic acids are so closely analogous to coumalinic acid; and considering, lastly, the readiness with which coumalinic acid is prepared from malic acid, and may be transformed into pyridine derivatives: it seems probable that the acids in question bear a close genetic relation to malic acid, coumalinic acid, and the pyridine compounds derived from them. Hence the formation of pyridine derivatives from malic acid is of interest from the point of view of vegetable physiology, and affords experimental material which may serve to explain the natural formation of the alkaloids.

The study of the products obtained by the action of ammonia and amido-compounds on coumalinic acid has led to an explanation of their constitution, and affords an insight into the method of their formation. On account of its instability, coumalinic acid is not well adapted for the investigation of this reaction, but the methyl salt described in a previous communication furnishes almost quantitative results.

Ammonia and coumalinic acid, in the form of one of its ethereal salts, as already explained, form a hydroxypyridinecarboxylic acid (hydroxynicotinic acid), which it will be proved has the constitutional formula—



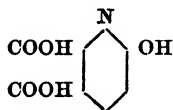
and which is identical with that prepared by Koenigs and Geigy (*Ber.*, 1884, 589) from hydroxyquinolinic acid by elimination of carbonic anhydride. Koenigs and Körner (*Ber.*, 1883, 2152) have proved that when cinchoninic acid is fused with potash, a hydroxyl-group attaches itself to the carbon-atom next to the nitrogen of the pyridine-ring, and from this Koenigs and Geigy have inferred that the hydroxyl-group likewise takes the same position in the hydroxyquinolinic acid prepared by an analogous reaction from quinolinic acid; this conclusion has been confirmed by investigation.

According to Friedländer and Ostermaier (*Ber.*, 1882, 332), in the chloroquinoline prepared by the action of phosphorous pentachloride on carbostyryl, the chlorine is readily displaced by H, C₂H₅O, &c., a behaviour which is characteristic of pyridine-derivatives in which the radicle is represented as contiguous to the nitrogen-atom. Now since hydroxypyridinecarboxylic acid can be converted into a chloro-pyridinecarboxylic acid of which the chlorine-atom is characterised by the same mobility as that of the chloroquinoline in question, it follows that this atom in the formula of the chlorinated acid, and the corresponding hydroxyl-group in the hydroxypyridinecarboxylic acid, likewise occupy the position contiguous to the nitrogen.

Finally, since the pyridinecarboxylic acid obtained from chloro-pyridinecarboxylic acid by displacing the chlorine by hydrogen has been proved to be identical with nicotinic acid, and in this it is certain that the carboxyl-group and the nitrogen are relatively in the position N:COOH = 1:3, there remains for hydroxynicotinic acid only the choice between the two following formulæ:—

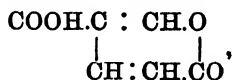


Of these, the first must be the correct one, as it alone explains the formation of this acid from hydroxyquinolinic acid,

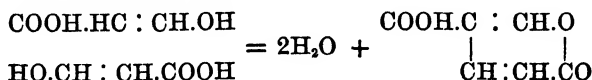


It now remains to explain how coumalinic acid is converted into hydroxynicotinic acid.

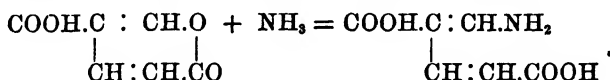
Although the correctness of the following formula for coumalinic acid,



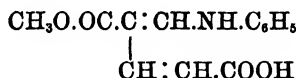
proposed by one of us in a former communication, has not yet been experimentally proved, it may be provisionally used, since no observations hitherto made on the acid are irreconcilable with it. The production of such a compound from the half-aldehyde of malic acid, $\text{COH} \cdot \text{CH}_2 \cdot \text{COOH}$, may be supposed to consist in the conversion of the aldehyde—by the alternate addition and loss of water—into a body of the composition $\text{CH}(\text{OH}) \cdot \text{CH} \cdot \text{COOH}$, of which two molecules condense in the following manner:—



The formation of hydroxynicotinic acid from coumalinic acid may be supposed to take place in two stages; in the first place, the elements of ammonia are added to the coumalinic acid, whereby the latter is transformed into an amido-acid, coumalamic acid:—

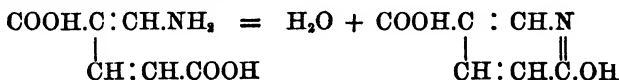


Although the instability of this compound prevents its isolation, there can be no doubt of its existence, since it is possible to prepare coumalanilidic acid, or rather its acid methyl salt, a perfectly analogous intermediate product formed by the action of aniline:—

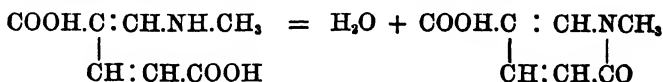


This substance has also been analysed.

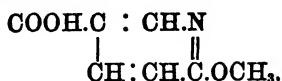
In the second phase of the reaction, coumalamic acid loses water, forming hydroxynicotinic acid:—



It might be expected that coualmethamic acid, the primary product of the action of methylamine, would resemble pseudoisatin in its behaviour, and would undergo the following change:—



It has been found, however, that the product of this reaction is identical with the methyl salt of the acid obtained by methylating hydroxynicotinic acid,



To explain this fact, it is necessary to assume a movement of the methyl-group from the nitrogen to the oxygen of the neighbouring ketone-group. This intramolecular change acquires additional interest from the analogous observations which Lieben and Haitinger (*Ber.*, 1884, 1507) have made on chelidonic acid and its pyridine-derivatives, showing that the parallelism existing between chelidonic and coumalinic acids may be extended to these characteristic features.

Hydroxynicotinic Acid,



The formation of this acid, and of its ethereal salt, always takes place when ammonia, or an aqueous solution of ammonium carbonate, is brought in contact with coumalinic acid or its ethereal salt. On account of its instability in alkaline solution, coumalinic acid yields but traces of nitrogenous substances; an abundant yield may, however, be obtained from its acid ethereal salts. If, for example, the methyl salt be mixed with dilute ammonia, and the excess of the latter be removed by boiling or allowing the fluid to remain at the ordinary temperature, colourless needles of the methyl salt of hydroxynicotinic acid are obtained. The following is the best process of preparing hydroxynicotinic acid:—1 part of finely powdered coumalinic acid is gradually added to a cold 15 per cent. solution of ammonia, and as soon as it is dissolved 6 parts of caustic soda solution (1 to 5) is added, and the whole boiled for five minutes. On adding concentrated hydrochloric acid to the cool solution, hydroxynicotinic acid separates out in the form of a colourless, heavy, crystalline powder, which may be purified by recrystallising it from 50 per cent. acetic acid. The acid may be obtained in colourless needles by recrystallisation from boiling water to which animal charcoal has been added:—

	Calculated for $\text{C}_6\text{H}_5\text{NO}_3$.	Found.
C	51.8	51.5 per cent.
H	3.6	3.9 "
N	10.1	9.5 "

The acid melts at 303° , becoming discoloured and evolving gas, but it may be sublimed by carefully heating. It is sparingly soluble in boiling water, almost insoluble in alcohol, ether, chloroform, and benzene, but more easily soluble in acid liquids. It has no basic properties,

and can be recrystallised from concentrated hydrochloric acid without undergoing any change. Its aqueous solution gives no precipitates with metallic salts in the cold, but on boiling with copper acetate a light green copper salt separates out. The alkaline salts crystallise well, the lead salt forming white needles containing water of crystallisation. Ferric chloride does not give any characteristic reaction.

On heating it with zinc-dust, pyridine is formed in large quantities. If the acid is heated to a temperature above its melting point, it splits up into carbonic anhydride and hydroxypyridine, $[N:OH = 1:2]$, which is also obtained by the action of hydrochloric acid at 200° , or by distilling the silver salt. The hydroxypyridine gives a reddish-yellow coloration with ferric chloride, and with bromine-water a brominated derivative, crystallising in needles and melting at 206° .

All these facts confirm the identity of the hydroxynicotinic acid with the hydroxypyridinecarboxylic acid of Koenigs and Geigy.

Chloronicotinic Acid, $C_6H_3NCl.COOH$.

If three molecular proportions of phosphorous pentachloride are gradually added to hydroxynicotinic acid covered with phosphorous oxychloride, and the mixture is heated at $120-130^{\circ}$, an energetic reaction takes place, and the substance dissolves. On pouring the product of the reaction into ice-cold water, the chlorinated acid separates out as a voluminous crystalline mass, which may be purified by recrystallising from hot water. The yield is theoretical:—

	Calculated for $C_6H_3NClO_3$.	Found.
C	45.7	46.1 per cent.
H	2.6	2.8 "
N	8.8	8.7 "
Cl	22.5	22.1 "

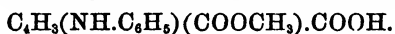
On carefully heating it, the acid sublimes, and melts at 199° with decomposition. It is much more easily soluble in water than the hydroxy-acid, crystallising from it in shining plates; it is also easily soluble in ether, alcohol, and glacial acetic acid, sparingly in chloroform and benzene. It is easily dissolved by concentrated hydrochloric acid, but separates out again on diluting with water. The aqueous solution gives a light green precipitate with copper acetate, especially when hot. By boiling with alcoholic potash, as well as by the action of reducing agents, substances are obtained which are free from chlorine.

Nicotinic Acid, $C_6H_4N.COOH$.

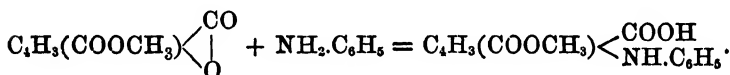
The best way of transforming the chloronicotinic acid into nicotinic acid is by the action of tin and hydrochloric acid. It is heated on the

water-bath until a sample remains clear on addition of water, which, if 5 grams be used, is the case after 15 to 20 minutes. The excess of hydrochloric acid is then got rid of, and the residue is dissolved in water, the tin removed by means of sulphuretted hydrogen, and the solution made slightly alkaline with soda and then boiled with copper acetate. Copper nicotinate is thus obtained as a greenish-blue precipitate, which, after being well washed, is suspended in water, and decomposed with sulphuretted hydrogen. On evaporating the filtrate, slender needles separate out, which melt at 229° , and exhibit all the reactions of nicotinic acid.

Monomethyl Salt of Coumalanilidic Acid,



This well characterised substance may serve as a type of the compounds formed by the action of primary amines on the ethereal salts of coumalinic acid. It is formed as represented by the equation



Bases such as methylamine, ethylamine, and glycocine, form in this way colourless addition-products, whereas the amido-compounds of the aromatic series, as, for example, aniline, toluidine, phenylhydrazine, amidobenzoic acid, and amidoquinoline, give yellow-coloured bodies.

For the preparation of the new compound, the methyl salt of coumalinic acid in alcoholic or dilute acetic acid solution is treated with aniline. If the degree of concentration be rightly gauged, the whole liquid after some moments becomes a solid mass of yellow crystals, a considerable amount of heat being developed. By one recrystallisation from hot alcohol, the substance is obtained in the form of lemon-yellow needles, sufficiently pure for analysis.

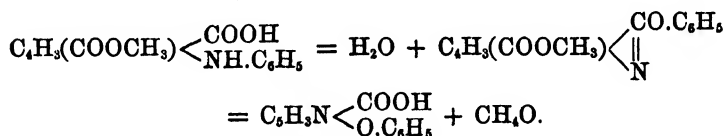
	Calculated for $\text{C}_{13}\text{H}_{13}\text{NO}_4$.	Found.	
C	63.16	63.1	62.9 per cent.
H	5.3	5.6	5.8 "
N	5.7	5.75	5.8 "

It melts at 140° with frothing. It is easily soluble in hot alcohol, chloroform, and benzene, sparingly in ether, and insoluble in water. It has the properties of an acid, and dissolves in cold solutions of the alkaline carbonates with a yellow colour, from which solution it is precipitated unchanged by acids. It has no basic properties.

This compound is characterised by the readiness with which it undergoes change. When boiled with alcohol, it is transformed into a colourless, beautifully crystalline body, which is insoluble in alkalis. It also undergoes decomposition by the action of water, acids, or alkalis; on heating it with concentrated ammonium carbonate or sodium acetate, the solution which at first is clear becomes milky, and colourless drops of oil separate. Of these products, only the one obtained by the action of soda has been studied, namely, the acid phenyl salt of hydroxynicotinic acid.

Phenoxynicotinic Acid, $C_6H_5N(OC_6H_5).COOH$.

This acid is formed from the amido-methyl salt just described by boiling it with a moderate amount of soda until the addition of acid to a sample of it causes the formation of a white precipitate after the lapse of a few minutes. The reaction consists in the passage of the phenyl from the nitrogen to the oxygen, of the saponification of the methyl salt, and at the same time of the elimination of the elements of water; this takes place as represented by the equation—



That the acid really has this constitution follows from the analogous and already mentioned mode of formation of methoxynicotinic acid. If the compound which separates out from the alkaline solution when completely decomposed by hydrochloric acid, is recrystallised from boiling water, it forms white needles which melt at 275—280°.

	Calculated for $C_{12}H_9NO_3$.	Found.
C.	67.0	67.0 per cent.
H	4.2	4.6 ,,
N	6.5	6.4 ,,

On carefully heating the substance, it sublimes in the form of characteristic voluminous needles, which resemble cotton-wool. It is soluble in hot water, alcohol, and glacial acetic acid, but almost insoluble in ether, chloroform, and benzene; on adding water to its solution in concentrated hydrochloric acid, it is precipitated unchanged. If the aqueous solution is boiled with copper acetate, a sparingly soluble precipitate is formed. On heating it with concentrated hydrochloric acid at 200°, carbonic anhydride is eliminated and a body formed which crystallises beautifully from ether; this

is insoluble in alkalis, and seems to be the phenyl ether derived from hydroxypyridine. This compound would consequently be as stable as the phenyl ether, $(C_6H_5)_2O$.

Methoxynicotinic Acid, $C_6H_5N(OCH_3).COOH$.

This acid, as already stated, can be obtained either by methylating hydroxynicotinic acid or from methylamine and coumalinic acid.

In preparing it from the hydroxy-acid, 3 grams were taken and evaporated to dryness with two molecular proportions of potassium hydroxide, and the finely powdered mass was then heated for three hours at $100-110^\circ$ with methyl alcohol and methyl iodide. After opening the tubes, the methyl alcohol and excess of iodide were expelled by boiling the contents, which were then made slightly acid and the product twice crystallised from boiling water.

To obtain this compound synthetically, the methyl salt of coumalinic acid is added to 4 parts of a 15 per cent. methylamine solution, which is kept cool and then immediately boiled with 5 parts of caustic soda solution (1.5) till completely saponified. When cold, it is carefully acidified and twice crystallised from water. The monomethyl salt of coumalmethamic acid, which may be regarded as an intermediate product, separates out on careful dilution of the solution of the monomethyl salt of coumalinic acid in methylamine in the form of colourless, easily soluble, crystalline needles.

By both methods, methoxynicotinic acid is obtained in very characteristic flattened needles, which contain a molecule of water of crystallisation; they lose the same, however, in a vacuum or at 100° , and become opaque.

	Calculated for $C_7NH_7NO_3 + H_2O$.	Found.
H_2O	10.5	10.5 per cent.

The dried substance gave the following numbers, of which those under I are from the hydroxy-acid, and those under II from material synthetically prepared.

	Calculated for $C_7H_7NO_3$.	Found.	
		I.	II.
C	54.9	54.8	55.3
H	4.6	4.5	4.6
N	9.1	9.6	—

Melting point $237-238^\circ$. The acid is almost insoluble in cold water, but dissolves so readily in boiling water that, as a rule, a hot saturated solution on cooling solidifies to a thick mass of crystals.

It is soluble in alcohol, ether, and glacial acetic acid, insoluble in chloroform and benzene. It has scarcely any basic properties.

The investigation will be continued and extended to other fatty acids.

XXII.—*On Nitrobenzalmalonic Acids.*

By CHARLES M. STUART, M.A., Fellow of St. John's College, Cambridge.

IN a former communication (Trans., 1883, p. 409), I mentioned that I had obtained an acid by the condensation of orthonitrobenzaldehyde with malonic acid, and at that time I believed it was not an unsaturated acid. The following account will show that the statement requires correction.

In order to prepare the acid, a mixture of orthonitrobenzaldehyde with sodium malonate and glacial acetic acid is allowed to remain for a few days at the ordinary temperature; it is then treated with water, and the excess of aldehyde removed by means of ether; after the addition of hydrochloric acid to the aqueous solution, the new acid may be dissolved out by agitation with ether. It may, however, be prepared more expeditiously as follows:—

A mixture of glacial acetic acid, malonic acid, and orthonitrobenzaldehyde is warmed for eight hours at 60°, water is then added, and any precipitate of unchanged orthonitrobenzaldehyde is filtered off. The aqueous solution is extracted with ether, and the residue left on distilling off the ether is evaporated with water on the water-bath, to remove acetic acid. The impure acid thus obtained may be purified as follows:—It is dissolved in ether, and carbon bisulphide added till the colouring matter, but not the acid, is precipitated; it is then filtered, and more bisulphide is added to the clear solution, when the acid crystallises out well; it still contains a trace of malonic acid, but this may be removed by recrystallising it from water, from which it separates in needles.

Of a specimen submitted to analysis—

0.3578 gram gave 0.0992 gram H_2O and 0.6647 gram CO_2 .

0.5016 „ 26 c.c. nitrogen at 14° C., and 762 mm. pressure.

	Found.	Theory for $C_{10}H_7NO_6$.
C.	50.66	50.65
H	3.08	2.95
N	6.10	5.90

The silver salt was also prepared by neutralising a solution of the acid with ammonia, and precipitating with silver nitrate. On analysis—

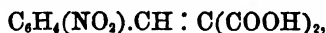
0.5938 gram gave 0.5877 gram CO_2 and 0.0721 gram H_2O .

0.4202 „ 0.2641 „ AgCl .

0.3267 „ 0.2066 „ „

	Theory for $\text{C}_{10}\text{H}_5\text{NO}_6\text{Ag}_2$	Found.	
		I.	II.
C	26.60	26.99	—
H	1.10	1.34	—
Ag	47.89	47.35	47.59

The acid is therefore orthonitrobenzalmalonic acid,



and is isomeric with the paranitrobenzalmalonic acid described in my previous paper. It melts at 161° with evolution of carbonic anhydride and carbonisation; it dissolves readily in water, is very soluble in ether, sparingly in chloroform, and insoluble in benzene and carbon bisulphide; it gives a red colour when warmed with concentrated sulphuric acid.

Barium Salt.—If a solution of the acid is neutralised with ammonia, and barium chloride is added, a very beautiful salt is deposited in white feathery tufts; this salt, however, cannot be recrystallised, as when it is warmed with water, it is at once converted into another salt, consisting of small hard insoluble nodules.

Of the feathery tufts submitted to analysis—

0.2147 gram lost at 120° 0.234 gram, and gave 0.1187 gram barium sulphate.

	Theory for $\text{C}_{10}\text{H}_4\text{NO}_6\text{Ba}, 2\frac{1}{2}\text{H}_2\text{O}$	Found.
H_2O	10.79	10.89
Ba	32.85	32.50
Calculated for dry salt.		Found.
Ba	36.81	36.48

Of the hard nodules submitted to analysis—

0.5208 gram dried at 130° gave 0.3096 gram BaSO_4 .

0.681 „ „ 160° „ 0.4083 „ „

	Theory for $\text{C}_{10}\text{H}_4\text{O}_6\text{Ba}, \text{H}_2\text{O}$	Found.	
		I.	II.
Ba	35.12	34.95	35.26

As the acid obtained from these two salts was the same, they are obviously two barium salts of orthonitrobenzalmalonic acid, containing different amounts of water of crystallisation; that of the latter is not given up at 160°.

The chief point of interest about this acid is its remarkable stability; whilst benzalmalonic acid, its paranitro-derivative, and, as we shall see later, its metanitro-derivative, are decomposed by boiling with water, orthonitrobenzalmalonic acid can be boiled for any length of time with dilute acids, without undergoing the slightest decomposition. I had indeed expected that the presence of the nitro-group in the ortho-position would increase the stability to such an extent as to enable me to extract a hydroxy-acid of the composition



in accordance with Baeyer and Einhorn's results quoted in my previous paper. The results show that although the stability is very materially increased by the presence of the nitro-group, yet no hydroxy-acid is obtained.

Having thus obtained and compared benzalmalonic acid with its ortho- and para-nitro-derivatives, it appeared to be of interest to prepare the metanitro-derivative, and observe its properties.

Equal weights of metanitrobenzaldehyde and malonic acid were heated with glacial acetic acid at 60°; in a few hours the mixture became almost solid from the formation of crystals; these were drained from acetic acid by a filter-pump, recrystallised from hot water, and washed with chloroform to remove metanitrobenzaldehyde.

Of a specimen submitted to analysis—

0.4067 gram gave 0.7576 gram CO_2 , and 0.1127 gram H_2O .

	Theory.	Found.
C.....	50.65	50.79
H	2.95	3.07

It is therefore metanitrobenzalmalonic acid. It melts at 205° with evolution of carbonic anhydride, leaving a residue of metanitrocinnamic acid melting at 196°.

It dissolves readily in hot water, being at the same time partially decomposed into metanitrobenzaldehyde, which accompanies the acid as it crystallises, and malonic acid, which can be extracted from the mother-liquors; it is only slightly soluble in cold water and ether; dissolved in ammonia, it gives precipitates of acicular crystals with solutions of barium and of calcium chloride.

I now wished to ascertain which of these acids would be produced by the direct nitration of benzalmalonic acid, but it was found that on adding benzalmalonic acid to fuming nitric acid cooled with ice,

rapid oxidation took place, with evolution of red fumes. On pouring the solution into water, paranitrobenzaldehyde and paranitrobenzoic acid, melting at 240° , were obtained. It was therefore resolved to nitrate the ethyl salt.

The ethyl salt, prepared by boiling benzalmalonic acid with alcohol and strong sulphuric acid, was distilled in a vacuum. The properties of this salt have been described by Claisen (*Ber.*, **14**, 348; and *Annalen*, **218**, 129). It was added to fuming nitric acid, cooled with a mixture of ice and hydrochloric acid, and the solution poured into ice-cold water; a crystalline precipitate settled, which was washed with sodium carbonate and sodium hydrogen sulphite solutions, and crystallised from alcohol.

The first crop of crystals consisted of fine long prisms, melting at 93° .

On analysis—

0.4166 gram gave 0.1824 gram H_2O , and 0.8758 gram CO_2 .

0.351 ,, 15.2 c.c. N at 13° and 748 mm. pressure.

	Found.	Theory.
C.....	57.33	57.33
H	4.86	5.11
N	5.02	4.77

On saponification, by boiling with a mixture of equal parts of glacial acetic acid, strong sulphuric acid, and water, paranitrobenzalmalonic acid (melting at 227° with evolution of carbonic anhydride) was obtained.

The second crop of crystals consisted of rhombs, which after recrystallisation melted at 53° , and upon saponification in the same way, give the orthonitrobenzalmalonic acid described above.

On analysis—

0.3778 gram gave 0.7897 gram CO_2 , and 0.1726 gram H_2O .

0.2705 ,, 11.8 c.c. at 13° and 739 mm. pressure.

	Found.	Theory.
C.....	57.00	57.33
H	5.07	5.11
N	5.00	4.77

From 11 grams of ethyl salt, 6.3 grams of the para- and 2.8 grams of the ortho-nitro-salt were obtained, being 48 and 21 per cent. of theory respectively. This is worthy of notice, because ethyl cinnamate on nitration gives 40 per cent. of the para- and 60 per cent. of the ortho-nitro-compound; whereas ethyl benzalmalonate, nitrated by acid cooled only with ice, gives but a trace of the orthonitro-derivative,

and when the acid is cooled by a freezing mixture the ortho-compound is produced in the small proportion mentioned above.

I am proceeding to investigate the additive compounds of these acids, which seem to promise something of interest.

XXIII.—*On Chemical Changes in their Relation to Micro-organisms.*

E. FRANKLAND, D.C.L., M.D., LL.D., F.R.S.

[A Lecture delivered before the Chemical Society on Thursday, February 5.]

IN addition to analytical and synthetical changes in chemical composition depending upon heat, light, and electricity, there are two well recognised kinds of chemical action, viz. :—

1. Chemical change effected in each of two or more substances brought into contact with each other; and,

2. Chemical change effected by contact with a substance which itself suffers apparently no alteration. Failing any satisfactory explanation, very heterogeneous changes of the latter kind have been grouped together under the designation of “catalytic actions,” but a careful study of many of the reactions of this second class has transferred them to the first, and it is more than probable that the remainder, when better known, will be similarly disposed of. The chemical changes occurring in animal and vegetable organisms were, until recently, tacitly, if not formally, relegated to the second type. The plant or animal was regarded either as effecting the changes by mere contact, or by some mysterious process outside the ken of experimental inquiry. This illusion has been finally dispelled by the synthetical operations of organic chemistry, which have taught us how to produce, by purely laboratory processes, numerous compounds formerly obtainable only as the products of living organisms, and it is to be hoped that chemists and biologists will now give more attention to this hitherto neglected field of chemical action—the chemical changes which occur in animal and vegetable organisms.

In studying the present aspect of this subject, I have found it neither desirable nor possible to draw any sharp line of demarcation between living beings of the highest type and the micro-organisms to which my remarks must be chiefly directed; in the first place, because I do not find any essential difference between the chemical changes which occur in man and the mammalia, for instance, and

those which accompany the lowest forms of life; and, secondly, because it is more than probable that many of those changes with which we are familiar in the bodies of the higher animals (and possibly in plants) are also brought about by micro-organisms.

The chemical actions induced by living organisms are of two kinds:—

1. Synthetical; and,
2. Analytical.

The first are chiefly performed by plants; the second by animals.

Of the synthetical operations the transformations of CO_2 , OH_2 , and NH_3 into cellulose, starch, sugar, gum, and albumen are the most conspicuous, although Hoppe-Seyler has observed synthetical changes under the influence of certain micro-organisms, as, for instance, the transformation of glycerin into hexyl alcohol and caproic acid after two years' putrefaction, 6-carbon molecules being thus produced from 3-carbon molecules. He considers that glycerin is first converted into lactic acid, and the synthesis is then performed by the combination of lactic acid residues. In his opinion, animal fats are thus produced from carbohydrates. All the first named synthetical operations must be attended by the absorption of heat; or, in other words, by the transformation of actual into potential energy.

What is the nature of the substance in the plant which decomposes CO_2 and OH_2 , liberating C under the influence of solar or artificial light? Scarcely any approach has yet been made towards the answer to this question, and yet it cannot be doubted that a satisfactory reply will sooner or later be disclosed. Has the vegetable kingdom the monopoly of the substance which effects this transformation? This is scarcely probable, for although the secret has eluded chemical research half a century beyond the time when Wohler and Kolbe found out the artificial synthesis of organic compounds, yet it cannot be doubted that it belongs to the "knowable," and will be discovered. As a step towards the solution of this problem, it was interesting to ascertain whether, under the influence of a powerful beam of light, the constituent atoms of CO_2 and OH_2 molecules become to any extent dissociated as they do under the influence of a high temperature. In other words, can the luminous impulses compel these atoms to make excursions beyond the molecular boundary of their mutual attractions? To put this to the proof, I exposed CO_2 , both alone and mixed with aqueous vapour, in an extreme state of attenuation to the intense light of a powerful electric arc, but failed to detect the slightest decomposition. I then similarly exposed a mixture of carbonic anhydride and nitric oxide, but even this searching test for wandering atoms of oxygen failed to detect any. Although light has not yet been made to produce these results, it is well known that they

can be effected by electricity, and that not merely by the disruptive discharge or by electrolysis, but by the silent discharge. It is now more than a quarter of a century since I saw, in Gassiot's laboratory, the vacuum of a water-hammer impaired by silent discharges induced from without; this result having been brought about by the decomposition of the aqueous vapour inside the glass tube. Brodie has since demonstrated that CO_2 is decomposed into CO and O by the same means.

The *modus operandi* of plants in effecting chemical changes being at present entirely unknown, we cannot with profit pursue the discussion of the vegetable division of organic life. I therefore propose to confine our attention to the chemical operations of animal life. Here, however, I am met by the difficulty of distinguishing between plants and animals amongst micro-organisms. Biologists have not yet arrived at a final conclusion as to the definitions which shall completely separate the animal from the vegetable kingdom. For our present purpose the following definitions will be sufficient:—

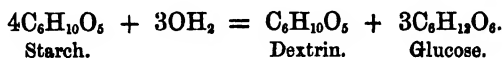
1. A plant is an organism performing synthetical functions, or one in which these functions are greatly predominant.
2. An animal is an organism performing analytical functions, or one in which these functions greatly predominate.

From a *physical* point of view the distinctive characteristics of plants and animals may be thus formulated—a plant is an organism which transforms actual into potential energy, whilst an animal is one which transforms potential into actual energy.

So far as I have been able to make out, all micro-organisms belong to the second class. Their life depends essentially upon the taking asunder of more or less complex compounds, resolving them into simpler molecules at the expense of potential energy. The new and simpler molecules, therefore, contain less potential energy than those from which they are derived. As micro-organisms are commonly termed ferments, and their analytical operations fermentation, it is necessary here to distinguish, sharply, between these organised ferments and certain other bodies which bring about analogous chemical changes, but which are not only unorganised, but invariably exist in solution. These latter, or “soluble ferments,” as they are commonly termed, are said to act by contact; they produce certain chemical changes in organic compounds (the fermentescible substances) without themselves furnishing from their own substance any of the products of the reaction. In this way a comparatively minute quantity of the ferment can effect the transformation of a very large quantity of the fermentescible substance. As we proceed, it will be seen that these soluble ferments are essentially analytical, and that their effects are closely allied to those of the organised ferments, differing only or

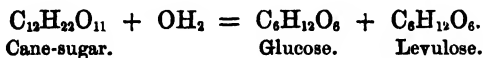
chiefly from them in the absence of organised matter, and in the non-increase of the ferment during its action upon the fermentescible substance. I will, therefore, here briefly indicate those fermentations which are the results of so-called contact action, and not of micro-organisms:—

1. Transformation of starch into glucose and dextrin, or hydrated maltose by diastase—



Hoppe-Seyler gives this equation. The identity of this glucose with grape-sugar has been called in question by Nasse.

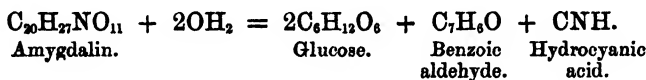
2. Transformation of cane sugar into glucose (dextrose) and levulose—



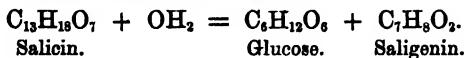
Berthelot has shown that this change is effected by a soluble ferment accompanying yeast, and also found in the bodies of bees and in bee-bread. It has been named "Invertin."

3. The transformation of glucosides:—

(a.) Amygdalin into glucose, benzoic aldehyde, and hydrocyanic acid—



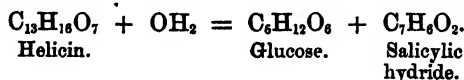
(b.) Salicin into glucose and saligenin—



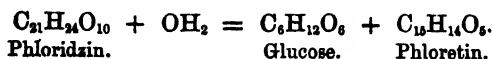
(c.) Arbutin into glucose and hydroquinone—



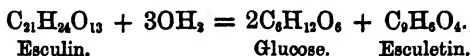
(d.) Helicin (product of the oxidation of salicin) into glucose and salicylic hydride (product of the oxidation of saligenin)—



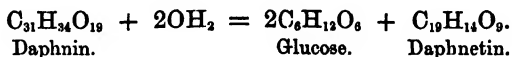
(e.) Phloridzin (in bark of apple and pear trees) splits into glucose and phloretin—



(f.) Esculin (in horse-chestnut bark) into glucose and esculetin—



(g.) Daphnin (in bark of the Mazereon) gives glucose and daphnetin—



All these reactions are produced by emulsin or synaptase, and many of them by yeast and other soluble ferments (salicin, helicin, and daphnin). Except in the case of amygdalin, acids produce the same results.

Of the same nature, appear to be the so-called fermentations producing (a) essential oil of mustard $\left\{ \begin{array}{l} \text{C}_3\text{H}_5 \\ \text{S} \\ \text{CN} \end{array} \right.$, (b) gallic acid and glucose from tannin, (c) alizarin and glucose from rubian, (d) margaric acid and glycerin in the so-called pancreatic fermentation, (e) and the proteic fermentation by which protein bodies are dissolved in the stomach.

All these phenomena appear to be due to soluble, and consequently unorganised organic matters.

The equations show that they are all essentially of the same character. They all consist in the assimilation of water, and with one exception (which is, however, only apparent), the splitting up of the fermentescible substance into two or more new molecules, one of which is a saccharine body.

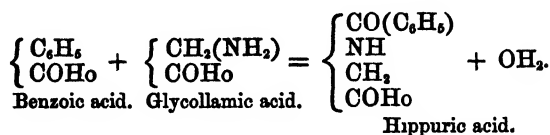
According to Müntz, these unorganised ferments can be sharply distinguished from organised by chloroform, which kills the latter, but has no effect on the former. Hamlet refutes this. P. Bert declares that compressed air in like manner distinguishes between the two.

Chemical Changes due to Micro-organisms.

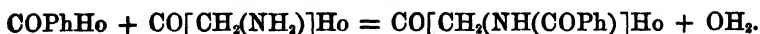
Having thus cleared the ground by the dismissal of a class of ferments which are soluble, and therefore not organised or living, we are now prepared to enter upon the chemical changes which are effected by living organisms:

In the higher animals, these transformations have not been studied in the systematic way that they deserve, nevertheless, some general and far reaching results have been established. Thus we know that the food which these animals consume is oxidised, and practically converted into carbonic anhydride, water, urea, hippuric acid, and ammoniac

urate, and that benzoic and kinic acids are converted into hippuric acid:—



or



With the exception of the last two, these changes are essentially processes of oxidation. In that portion of the animal world with which we are best acquainted, oxidation is the essential condition of life: it is the kind of action by which the animal changes *potential* into *actual* energy, and this actual energy is manifested in the phenomena which we term life. There are, however, many other chemical transformations in which potential becomes actual energy, and which therefore can support life. Besides such changes as are known to be thus utilised by micro-organisms, there are many others which might possibly be so utilised. It is even conceivable that animal life could be supported by allotropic or isomeric changes, analogous to the transformation of amorphous into waxy phosphorus, or of amorphous into crystalline antimony.

The changes effected by micro-organisms are essentially of the same character as those brought about by the higher orders of animals; that is to say, they are all changes by which potential becomes actual energy (as illustrated by the calorimetric determinations of Von Rechenberg), and these organisms appear to me, therefore, to be excluded from the vegetable kingdom, which is characterised by operations of the reverse order, attended with the transformation of actual into potential energy.

With one or two exceptions, the chemical changes effected by micro-organisms (unlike those produced by soluble ferments) cannot be brought about by other means. Thus the *direct* transformation of glucose into alcohol and carbonic anhydride, or into lactic acid, butyric acid, or gum, has not been accomplished except by vital operations, although some of these changes can be artificially effected by roundabout processes. Thus glucose can be resolved into its elements from which alcohol, lactic acid, and butyric acid can be constructed.

The conditions favourable and inimical to the propagation and development of micro-organisms have, of late years, received a good deal of attention. It has been established by Pasteur, that certain of these organisms, which he calls *aerobes*, can live only in the presence

of oxygen; whilst others, *anærobes*, continue their development only in the absence of this element, although their germs retain their vitality in aerated liquids and develop into active life, so soon as they come into an environment free from oxygen. The late Frank Hutton stated that, of the micro-organisms spontaneously developing during the putrescence of mutton broth, many survived 10 to 20 days under atmospheres of the following gases,—air, oxygen, nitrogen, hydrogen, carbonic oxide, carbonic anhydride, cyanogen, sulphurous anhydride, nitrous oxide, sulphuretted hydrogen, nitric oxide, acetylene, and coal-gas.

Some of these gases were utilised by the bacteria, whilst others were entirely unchanged. From air, the whole of the oxygen was absorbed and partially replaced by carbonic anhydride. Pure oxygen was slowly absorbed, and in 15 days more than one-fifth of it was converted into carbonic anhydride. Carbonic oxide was wholly absorbed, and partially converted into carbonic anhydride with evolution of hydrogen and marsh-gas. Cyanogen was to a considerable extent transformed into carbonic anhydride and nitrogen. Nitric oxide was partially absorbed and replaced by nitrogen and carbonic anhydride; but the bacteria did not attack this gas vigorously, for, at the end of 10 days, the greater part of it remained unchanged. Hydrogen, sulphurous anhydride, nitrogen, nitrous oxide, carbonic anhydride, acetylene, and coal-gas were unchanged.

Urea in aqueous solution, mixed with potassic phosphate, was decomposed with evolution of pure nitrogen. Solutions of salicylic acid, strychnine, brucine, morphine, and narcotine exerted no deleterious action upon these bacteria. On the other hand, they were rapidly destroyed by the following substances:—phenol, spongy iron, alcohol, and potassic permanganate. Kosegarten mentions thymol hydrocinnamic and phenylacetic acids, indole and scatole, as more or less inimical to the development, if not to the life, of bacteria. Most micro-organisms appear to retain their vitality under very wide ranges of temperature. It has not yet been shown that any degree of cold, however intense, is fatal. Animation may be suspended, but it is restored when the temperature rises. With regard to heat, the lowest fatal temperature recorded is 40° C., but many species can withstand much higher temperatures, and their germs retain their vitality after boiling for many hours, or even after exposure to a moist heat of 143° C. (Dallinger). They are, however, rapidly destroyed at a boiling temperature, if they have been previously softened by long maceration in warm water.

All these results lead to the conclusion that developed micro-organisms are very tenacious of life, whilst the vitality of their germs is even still more difficult to destroy. It is very desirable, however,

that researches of this kind should be extended in other directions. The unexpected fatal effects of spongy iron would seem to indicate that there are substances destructive to bacterial life but which have no toxic effect upon more highly organised animals. It has been suggested by Dr. James Johnson, that aromatic substances of various kinds may possess these properties, and hence their reputation as prophylactics, and their use in embalming, and in the preservation of animal and vegetable substances. It is needless to add how exceedingly valuable the discovery would be of substances virulent to micro-organisms and harmless to man.

I will now pass in brief review some of the best known micro-organisms and the chemical reactions due to them.

Yeast and its Chemical Reactions.

Yeast (*Saccharomyces cerevisiæ* or *Torula cerevisiæ*) consists of slightly egg-shaped cells filled with granules. Sometimes these cells are separate and sometimes strung together in chains of six or twelve,



Saccharomyces cerevisiæ
(Active cells.)



S. cerevisiæ.
(Exhausted cells.)

They are 0·009 mm. in their longest diameter and 0·008 in their shortest. They are "sprosspilze," that is, they multiply by budding, but sometimes by fructification or spores. The spores or cells are widely distributed in the air. They can propagate in water containing sugar, ammonia, and the necessary mineral constituents. Yeast is believed to obtain its carbon from sugar, and is probably incapable of decomposing carbonic anhydride. It contains no chlorophyll. Phosphorus is absolutely necessary for its development, and so is, probably, potassium. Deprived of free oxygen, yeast becomes inactive, but does not die for a long time. With excess of oxygen, it may vegetate without fermentation.

Yeast can withstand a temperature of nearly 100° C. when quite dry, but perishes at 53° when moist. It is comparatively insensitive to poisons, such as hydrocyanic acid, strychnine, antimony, phenol, and arsenious acid, but is destroyed by corrosive sublimate and sulphurous anhydride.

The following is the ultimate composition of yeast, after abstraction of ash:—

	Mitscherlich. Surface yeast.	Schlossberger.	
		Surface.	Bottom yeast.
C	47·0	49·9	48·0
H	6·6	6·6	6·5
N	10·0	12·1	9·8
S	0·6	—	—
O	35·8	31·4	35·8
	<hr/> 100·0	<hr/> 100·0	<hr/> 100·0
	<hr/> N : C = 1 : 4·7	<hr/> 1 : 4·1	<hr/> 1 : 4·9

Yeast is therefore a highly nitrogenous organism, containing a proportion of nitrogen approaching that present in protein, which contains N : C = 1 : 3·8.

The percentage of ash varies from 3·5 to 7·7, the chief constituents being potassic and magnesian phosphates.

Chemical Changes produced by Yeast.

1. *In Saccharine Bodies.*—The bodies of this class, which are *directly* subject to its action, are dextrose or glucose, levulose, maltose, and lactose or galactose.

Those which are only *indirectly* affected, that is, after transformation into glucose, are cane-sugar, melitose, trehalose, melezitose, starch, dextrin, gum, and glycogen.

The dominant, if not the sole, products of the action of yeast upon saccharine bodies are alcohol and carbonic anhydride—



If subject to this transformation alone, 100 parts of glucose ought to give—

CO ₂	48·89
EtHo	51·11
	<hr/> 100·00

Pasteur found that the weight of these products was only—

CO ₂	46.40
EtHo	48.51
	<hr/>
	94.91

The missing 5.09 parts are resolved into one or more of the following compounds:—

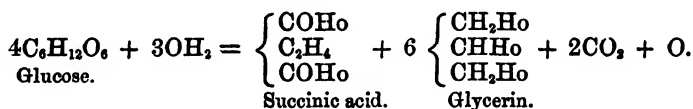
Propyl alcohol.	Glycerin.
Butyl ,,	Succinic acid.
Amyl ,,	Acetic acid.
	Butyric acid.

As part of the missing 5.09 parts, the following have been accounted for:—

Succinic acid and attendant CO ₂	1.13
Glycerin	3.00
	<hr/>
	4.13

leaving only 0.96 for the remaining products which have been qualitatively recognised, and for sugar forming new yeast cells.

According to Monoyer, the production of succinic acid and glycerin is explained by the following equation:—



No free oxygen has been detected; it may possibly acetify a minute portion of the alcohol.

The proportion of these bye-products is increased when fermentation is slow, and Horace Brown finds that fermentation is retarded under diminished pressure, and the proportion of carbonic anhydride to ethyl alcohol much increased.

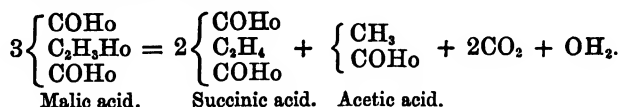
The question whether these bye-products are the work of the *Saccharomyces cerevisiae*, or each of a special organism, is highly important to the brewer, the wine grower, and the distiller. Perhaps also to the physician; for, closely connected with it, is another question, whether uric acid and other compounds, which may be considered as the bye-products collateral with urea, are generated by distinct species of micro-organisms in the blood.

Sugar of milk or lactose is not directly fermentescible by yeast, that is to say, it is not a food for yeast; but when submitted to the action of acids it is converted into two isomers, called *galactose*, both of which are fermentescible and behave like glucose.

By another micro-organism, which has not been further investigated, sugar of milk is directly converted into alcohol. This micro-organism is developed when milk is allowed to stand in wooden vessels, and the product is the koumiss of Tartary.

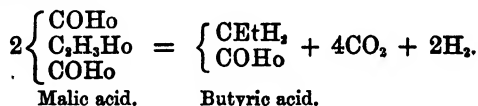
One part by weight of dry yeast transforms 100 parts of grape-sugar into alcohol and carbonic anhydride in from 6 to 10 days, or say, 10 times its weight in 24 hours. One part moist yeast transforms 2·6 parts of grape-sugar in 6 days, or about two-fifths of its weight in 24 hours.

2. *In Malic Acid.*—*Saccharomyces cerevisiae* breaks up malic acid into succinic acid, acetic acid, carbonic anhydride, and water, according to the following equation:—



The calcium salt is generally employed, and the most favourable temperature lies between 15° and 30° C.

Sometimes little or no succinic acid is formed, butyric acid taking its place. It has not been shown that this is not due to the prevalence of *Bacillus subtilis*:—

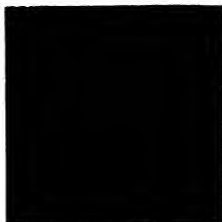


Theoretically 3 lbs. of calcic malate ought to give nearly 1½ lb. of succinic acid. Liebig actually obtained 1 lb. The transformation is therefore tolerably clean and sharp.

3. *In Glycerin.*—Retenbacher found that fermentation with yeast produced propionic and acetic acids; but this has since been denied by Roos and Brown.

Saccharomyces Apiculatus.

This is another alcoholic ferment which exists in ripe and juicy



Saccharomyces Apiculatus.

fruits, and winters in the earth. It develops in two forms, one lemon-shaped, the other more elliptical. It has only one-sixth of the activity of the *S. cerevisiæ*, and it produces beer of an entirely different flavour. It resists heat and moisture well.

Eurotium Oryzæ.

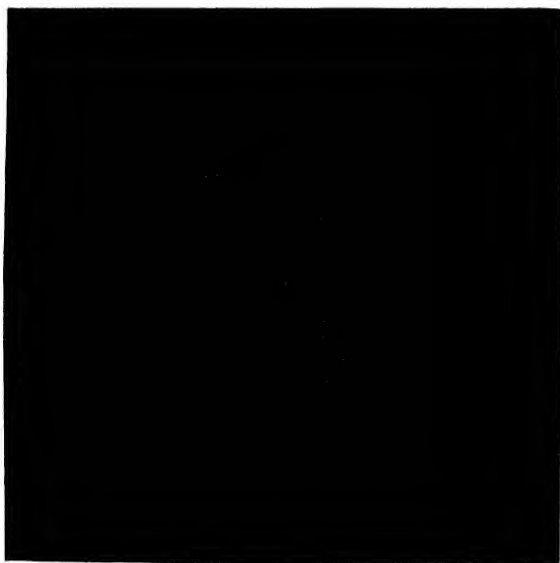
This alcohol-producing ferment is used in Japan for producing *Saki*.

Mucor Racemosus—*Mucor Mucedo*.

These micro-organisms also produce alcohol, but only in the absence of free oxygen. The spontaneous production of alcohol and carbonic anhydride from fruit, when excluded from the air, is probably due to one of these ferments.

These fermentations were first described by James Bell (to whom I am indebted for several of the microscopic drawings), and his observations have since been confirmed by Pasteur.

So far as experiments have gone, it would appear that the distinction between the effect of different alcoholic ferments is chiefly one of



Mucor Racemosus and *M. Mucedo*.

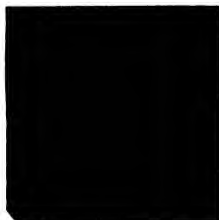
degree only The yeast organisms set to work with great energy, and diffuse themselves rapidly throughout the whole liquid, whereas the

action of the other organisms is more localised and consequently slower. These actions of the alcohol organisms, other than yeast, have, however, hitherto not been exhaustively studied as regards their subsidiary products.

Mycoderma Aceti.

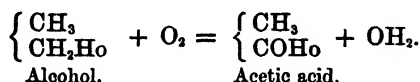
Acetic acid is one of the products of a number of fermentations. It is a product of the fermentation of calcic tartrate, malate, citrate, and mucate. It is produced from glycerin by yeast; from ethyl alcohol by muscle; from sugar by the lactic and butyric ferments, and from starch by the *leaven* ferment. It is also produced, probably by a micro-organism, during the germination of seeds.

The special organism, however, which transforms alcohol into acetic acid is the *Mycoderma aceti* (mother of vinegar), which forms a gelatinous mass resolved under the microscope into innumerable bent chain-like threads, which split by transverse section.



Mycoderma aceti.

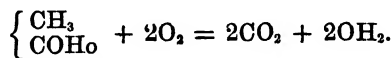
These filaments are usually accompanied by spherical cellules when the liquid becomes acid. According to Pasteur, the germs of this organism are everywhere in the air, and rapidly develop on the surface of weak alcoholic liquors containing nitrogenous matters and phosphates. The *Mycoderma aceti* flourishes as a film on the surface of the liquid, and, so long as it remains there, it determines rapid oxidation of the alcohol; but as soon as it is immersed, it becomes inactive and oxidation ceases. This points decidedly to true zymotic action, as distinguished from that of a soluble ferment. The reaction is:—



A little succinic acid is also formed.

Such is the oxidising power of this organism that, when all alcohol has been transformed into acetic acid, it immediately attacks what

must be regarded as its own excrement, and prolongs its existence by transforming acetic acid into carbonic anhydride and water.



Acetic acid.

Mycoderma aceti develops readily in weak alcohol to which small quantities of acetic acid, albumen, and alkaline phosphate, have been added. An excess of alcohol or acetic acid, or the withdrawal of oxygen by the immersion of the organism, promptly arrests all further production of acetic acid.

Fresh *Mycoderma aceti* contains 95 per cent. of water and only 5 per cent. of solid matter. The latter consists of 94 per cent. of organic matter and 6 per cent. of ash, which is chiefly phosphates.

100 grams of pure alcohol require, for conversion into acetic acid, 69.57 grams of oxygen; or 1 litre of pure alcohol requires 552.4 grams of oxygen, or about 2.1 cubic metres of atmospheric air, for its oxidation; but as only about one-fifth of the oxygen is used, it follows that more than 10 cubic metres of air must pass through the respiratory organs of the *Mycoderma aceti* in the transformation of 1 litre of alcohol into acetic acid.

The Lactic Bacillus.

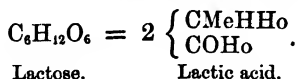
This micro-organism producing lactic fermentation somewhat resembles yeast. It consists of slightly viscous globules $\frac{1}{800}$ mm. in diameter, sometimes single and sometimes strung together in short chains. When single, these cells readily exhibit that molecular motion which is commonly called the Brownian movement. They appear to be a species of bacterium requiring no free oxygen for their



Lactic Bacillus.

development. They prefer a more dilute saccharine solution than that which is most favourable for yeast, and the continuous neutralisation of the lactic acid, as it is formed, also favours their development. The spores of this bacillus are everywhere in the air, and are believed

to be the cause of the souring of milk, by the transformation of milk-sugar into lactic acid in accordance with the following equation:—



On the other hand, A. Schmidt attributes the coagulation of milk to an 'unorganised ferment, which is precipitable by alcohol. When this precipitate is dissolved in water and added to milk, it produces rapid coagulation.

According to Bechamp, the coagulation of milk is due to micro-organisms contained normally in the liquid as it comes from the cow. They cause alcoholic, acetic, and lactic fermentation whether the organisms have developed into bacteria or not. According to this chemist, milk, as it comes from the cow, contains alcohol and acetic acid, and these increase as the milk becomes sour.

The saccharine bodies, sorbin, inosite, mannite, and dulcite, which are not attacked by yeast, yield at once to the lactic bacillus.

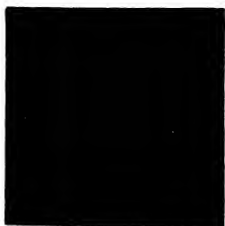
The lactic ferment is one of the most powerful enemies of the beet-root sugar manufacturer, as also, at times, of the wine grower.

The Butyric Bacillus (B. amylobacter).

In carrying out the usual fermentative process for the preparation of butyric acid from a mixture of milk, sugar, putrid cheese, tartaric acid and chalk, it has always appeared to me that as soon as the micro-organisms have transformed these materials into calcic lactate, they begin to attack the latter and prolong their existence by converting it into calcic butyrate with disengagement of hydrogen and carbonic anhydride, according to the following equation:—



In this equation, for the sake of simplicity, lactic acid is substituted for calcic lactate.



Butyric Ferment (Fitz).



Butyric Ferment (Bell).

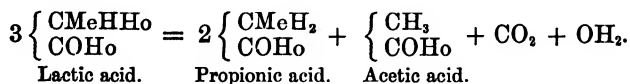
Bell and Fitz, however, describe a true butyric ferment which, according to the first named, consists of very active bacteria; but, according to the second, of round cells (arranged in garlands) 1·6 to 1·7 microns. in diameter. It is obtained by adding cow's excrement to calcic lactate. In a few days, the lactate is transformed almost entirely into normal butyrate, with traces only of acetic, caproic, and succinic acids. This is said to be the best ferment for butyric acid. I have sometimes obtained quite as good a result with cheese; but, on other occasions, a mixture of acids was produced from which it was difficult to extract any pure butyric acid.

Van Tieghem finds that *Bacillus amylobacter* always produces butyric acid, carbonic anhydride, and hydrogen, no matter what substance it operates upon. Thus, for instance, it always yields these products when it attacks cellulose, dextrin, arabin, lichenin, lactose, mannite, glycerin, calcic malate, or calcic citrate.



Bacillus Amylobacter (Tieghem).

On the other hand, when a small long bacillus, often in long bent chains, gains the victory, calcic lactate is converted into the calcium salts of propionic and acetic acids, according to the following equation:—



Glycerin Fermentation. Butyl bacillus and Ethyl bacillus.

Fitz has observed that there is a micro-organism which converts glycerin into normal butyl alcohol, normal butyric acid, caproic acid, and a small quantity of ethyl alcohol. The acids must be continuously saturated with calcic carbonate. A good result was obtained with the following mixture:—2000 parts of water, 100 of glycerin, 1 of potassic phosphate, 0·5 of magnesian sulphate, 2 parts of pepsin (as food for the ferment), and 20 parts of chalk. To this, a trace of the ferment was added, and the mixture exposed to a temperature of 40° C. The

micro-organisms increased rapidly, and after two days, energetic fermentation set in, and was finished in 10 days.

There were obtained about 7·7 of butyl alcohol per hundred parts of glycerin employed, and 12·3 per cent. of normal calcic butyrate. Also a small quantity of a non-volatile acid, probably lactic acid, and a base of the picoline type. If the butyl alcohol be distilled off, the fermentation will recommence without fresh ferment.

Fitz believes that two distinct organisms take part in this fermentation, one producing butyl alcohol, and the other ethyl alcohol. The ethyl bacillus appears to be identical with the *B. subtilis* of Cohn. It is a small thin bacillus which is coloured yellow by iodine, and is easily distinguished from the butyl bacillus, which is much broader (2 to 3 microms. broad, and 5 to 6 long), and is coloured violet, or even black, by iodine. The ethyl bacillus withstands a boiling temperature, whilst the butyl bacillus is destroyed by this temperature.



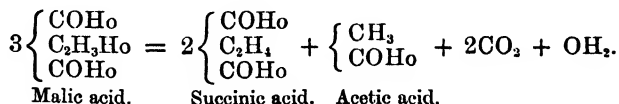
Butyl Bacillus.



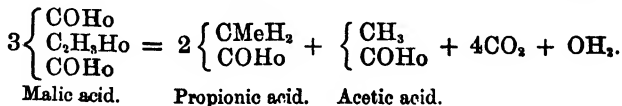
Bacillus Subtilis, Ethyl Bacillus (Cohn).

Malic Fermentation.

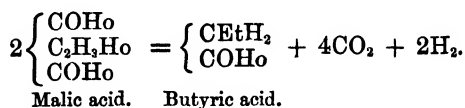
In addition to its fermentation by yeast, already alluded to, calcic malate is also attacked by the micro-organisms contained in putrid cheese or muscle. These organisms are "spaltpilsen," and appear to be of three different species. One of them, which has the appearance of small thin rods, produces succinic acid, thus:—



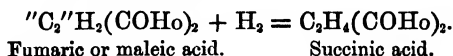
Another, which is a short cylindrical bacillus, splits the malic acid into propionic and acetic acids, carbonic anhydride, and water.



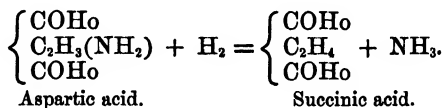
Whilst a third is the ordinary butyric ferment, taking the malic acid neatly asunder into butyric acid, carbonic anhydride, and hydrogen.



It is highly probable that the transformation of maleic and fumaric acid into succinic acid, by fermentation with putrid cheese, is performed by one of these organisms:—

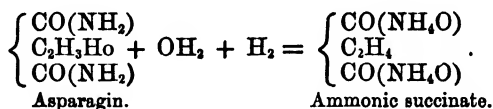


The transformation of aspartic acid into succinic acid and ammonia is also probably the work of the same organism:—



The calcium salts were used by Dessaignes, who observed these reactions.

The change of asparagin into ammoniac succinate is of the same type of fermentations.



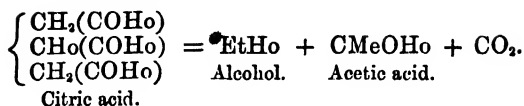
P. Miquel finds that asparagin is converted into carbonic anhydride, ammonia, and succinic acid by a bacterium existing in water. This organism is twice branched, 0·0015 mm. long, and 0·0008 mm. thick. It is destroyed by a temperature of 49° C.

Erythrite Fermentation.

This sugar can be fermented by cows' excrement, but the ferment should be several times cultivated in fresh solutions of erythrite. Many kinds of "spaltpilsen" are produced, the most prominent being pear-shaped cells which become elliptical towards the end of the fermentation. They are 1·5 microm. broad and 2·5—2·8 microms. long.

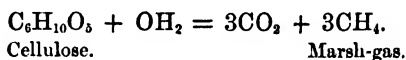
The products from 30 grams of erythrite were—

FRANKLAND ON CHEMICAL CHANGES



Cellulose Fermentation.

According to Böhm, the cellulose of land or bog plants undergoes, under water, a butyric fermentation, whilst the cellulose of aquatic plants splits up into carbonic anhydride and marsh-gas.



Glyceric Acid Fermentation.

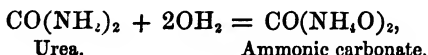
A peculiar bacillus causes fermentation in calcic glycerate, and produces ethyl and methyl alcohols, formic acid, and a little acetic acid. No non-volatile acid is produced.

Bacterium Termo.

This organism resolves tartaric acid into succinic acid, acetic acid, and carbonic anhydride; but if the calcium salt of this acid be presented to *Bacterium termo*, it is broken up into acetic acid, traces of propionic acid, formic acid, and carbonic anhydride.

Bacillus Ureæ.

This bacillus, or vibrio, which gets its living by converting urea into ammonic carbonate by the following reaction,—



continues in active motion until the change is complete, and then becomes motionless and probably dead.



Urea Bacillus.

According to Miquel this bacillus belongs to the class of aërobes, is 0·006 mm. long and 0·0008 mm. broad, and bears a heat of 90° C. It changes to elliptical spores which, even when moist, withstand a temperature of 96° C.

In order to study the action of this bacillus upon urea, I allowed fresh urine to stand for 25 days in a clean glass vessel, observing, at short intervals, the progressive development of micro-organisms, and determining at the same time the amount of organic carbon, organic nitrogen, and ammonia in 100,000 parts of the liquid.

The following results were obtained :—

	Residue left on evaporation and drying at 100° C.	Organic carbon.	Nitrogen as urea and other organic matter.	Ammonia.	Microscopical observations.
Fresh urine	4817·0	943·81	1080·27	142·40	No bacilli.
" " after 1 day..	—	940·46	1095·05	136·65	"
" " " 3 days.	—	928·76	1106·70	136·50	"
" " " 5 " "	—	882·66	983·26	288·55	No observation.
" " " 7 " "	—	739·82	900·80	333·60	Sparse bacilli.
" " " 9 " "	—	682·99	784·93	485·12	No observation.
" " " 11 " "	—	621·02	744·64	534·30	Numerous bacilli.
" " " 14 " "	—	559·22	481·49	870·62	Very numerous bacilli.
" " " 16 " "	—	530·68	492·04	881·87	Vast numbers of bacilli.
" " " 18 " "	—	487·01	355·25	990·78	Mostly still.
" " " 21 " "	—	466·43	278·22	1105·75	" "
" " " 23 " "	—	451·43	347·45	1017·25	All dead or still.
" " " 25 " "	2718·0	460·78	283·90	1070·50	" "
After allowing for evaporation	2045·5	346·77	213·66	805·63	

On the 5th day only, was any trace of nitric or nitrous acid present, and then only 0·019 part per 100,000.

The sample analysed on the 14th day was previously filtered; the others were all analysed unfiltered.

During the experiments, the liquid became considerably concentrated by spontaneous evaporation; for, whereas at the commencement it contained only 730·0 parts of chlorine, at the conclusion the amount found was 970·0 parts per 100,000.

The results of these observations and determinations, which were made during the month of June, show conclusively that, previously to the development of *Bacillus ureæ*, the chemical composition of the urine remained practically unchanged; but with the appearance of micro-organisms, a diminution of organic carbon and a transference of nitrogen from the organic to the ammonia column immediately

began. As regards rapidity, this change marched *pari passu* with the density of population, and reached its maximum about the 12th day; for during the three days (11th to 14th) nearly 10 per cent. of carbon disappeared, whilst more than 35 per cent. of the organic nitrogen became ammonia. After the 14th day, the rate of change became much slower, on the 18th day the bacilli were mostly either dead or motionless, whilst on and after the 23rd day no more moving bacilli were seen. Altogether, the quantity of carbon converted into carbonic anhydride, after allowing for concentration of the liquid by evaporation, amounted to 597.04 parts per 100,000 of liquid, or 63.3 per cent. of the total quantity; whilst the quantity of organic nitrogen converted into ammonia was 546.19 parts per 100,000, or 50.6 per cent. of the whole. These proportions show that all the organic nitrogen contained in the urea was not converted into ammonia. It no doubt escaped as free nitrogen, in accordance with Frank Hatton's observation.

In the original urine, the proportion of organic carbon to organic nitrogen was as 1:1.15, whilst, after the action of the bacilli, it was as 1:0.62.

Kinic Acid (C₇H₁₂O₆) Fermentation.

Spaltpilsen, when fed with asparagin, potassic phosphate, and magnesian sulphate convert kinic into protocatechuic acid, $\left(\begin{array}{c} \text{C}_6\text{H}_3\text{HO}_2 \\ \text{COHo} \end{array} \right)$, but if the organism be fed with peptone, no protocatechuic acid is produced, but the molecule of kinic acid is split up into formic, acetic, and propionic acids.

Hay Bacilli.

The action of the micro-organisms which convert grass into hay or ensilage has been studied by Mr. F. Jordan and my son. These organisms exist in vast numbers in grass. In the presence of free oxygen, they absorb this gas and evolve carbonic anhydride and nitrogen, and these are the gaseous products in the making of hay. The action is sufficiently energetic to set fire to the hay, if it is stacked too soon; but it is inconceivable that the bacilli continue their action until ignition ensues, and therefore ordinary oxidation probably supervenes.

The absorption of oxygen is not necessary, for carbonic anhydride is evolved in an atmosphere of hydrogen; but, under these circumstances, very little nitrogen makes its appearance.

The fermentation goes on under water, but its character is changed. The gases, which are much augmented in volume, now consist of carbonic anhydride (84.63 per cent.), hydrogen (6.9 per cent.),

nitrogen (5.83 per cent.), and traces of other combustible gas, probably marsh-gas. Acetic acid, lactic acid, and probably butyric acid are at the same time formed. This is probably the kind of fermentation by which grass is converted into ensilage.

Nitrification.

In respect of utility to man, few species of bacteria can claim precedence over the organism which, in the presence of bases, transforms nitrogenous organic matter into nitrates. This organism is the real natural scavenger of both savage and civilised society, and its operations are all the more acceptable because it transforms foul and offensive animal matter into innocuous and inodorous mineral compounds. It carries out to completion the work commenced by the *Bacillus ureæ*, and it is the great agent in the purification of sewage by irrigation and intermittent filtration. Unfortunately, it does not seem to prey upon morbid bacilli and their spores; otherwise, low as its place is in creation, it would, after man, be the most useful organism in existence.

Warington and Storer find that this bacterium works only in the dark, which again is an advantage, as the materials it operates upon are best kept out of sight. In the presence of bases, it transforms both nitrogenous organic matter and ammonia into nitrates, the most complete form of nitrogenous oxidation. It is also found that the formation of nitrites is determined by a modification of the nitrate bacillus. It is active in more concentrated solutions and at a higher temperature than 15° C. When once formed, this modified ferment always produces nitrites. It has no action on potassic nitrite, whilst the nitrate bacterium converts this into potassic nitrate.

I must not omit to notice the extraordinary selective power exhibited by some micro-organisms, and first observed and utilised by Pasteur, who employed a micro-organism to destroy one of the optically active compounds in a mixture, and thus to isolate the compound of opposite optical activity. He operated upon racemic acid, out of which the *Penicillium glaucum* consumed all the dextrotartaric acid, but preferred to die rather than to eat the lævotartaric acid. Le Bel afterwards extended these observations to optically active amyl alcohol and propyl glycol, whilst Lewkowitsch was the first who showed that by varying the micro-organism, either the dextro- or lævo-compound (in the case of mandelic acid) could be destroyed at will.

In conclusion, I have endeavoured to show that there are two classes of operations by which chemical changes in organic matter are

brought about in a somewhat mysterious way. Superficially considered, these classes appear to be nearly allied, but on closer study they are found to be essentially different.

In the first place, although a comparatively small amount of a soluble ferment can produce a chemical change in a large mass of matter, its action is limited; whereas there is no such limit to the action of an organised ferment. Thus the distiller finds that it is necessary to add 18 per cent. of malt in mashing, in order to convert the whole of the starch of the unmalted grain into sugar. But a single yeast cell, in an albuminous liquid, will bring about the conversion of an unlimited amount of sugar into alcohol.

Secondly, soluble ferments are unaffected in their activity by chloroform or compressed air, whilst these reagents at once arrest the changes produced by micro-organisms.

Thirdly, the changes effected by soluble ferments can, with scarcely an exception, be easily brought about by purely chemical means, whilst those dependent upon the presence of micro-organisms have, with one or two exceptions, never been directly effected by other non-vital means.

I have also hazarded the proposition that there is no break in the continuity of chemical functions between micro-organisms and the higher forms of animal life. Both alike owe their vitality to the liberation of the energy stored in their food, and both go through a cycle of existence and then lose their vitality. It is true that there are apparently certain sharp distinctions between them. Thus the enormous fecundity of micro-organisms and their tremendous appetites (on the assumption that all the changed matter passes through their bodies) seem to separate them from the higher orders of animals. But this distinction is only comparative.

Thus, in regard to fecundity, the power of multiplication gradually increases as the animal descends in the scale of organisation. There are, of course, exceptions, but this is the rule. The sheep produces only one or two lambs annually. The herring in the same time multiplies itself many thousand fold, whilst the aphid produces young at such a rate, that a single specimen would, if all its progeny lived, produce in three months a weight of aphides greater than that of the whole contemporary human race. And, as to appetite, voracity is greatest in the lowest organisms. A sheep or a cow consumes about one-sixth of its own weight in 24 hours; an earthworm, a caterpillar, or a silkworm many times its own weight. The yeast organism must, therefore, taking into account its position in nature, be considered decidedly abstemious, inasmuch as it only consumes two-fifths of its own weight of sugar in the course of 24 hours. Moreover, it must be borne in mind that the sheep converts most of its food into carbonic

anhydride, water, and hippuric acid, thus utilising nearly the whole of the potential energy, whilst the micro-organism, as a rule, utilises only a small portion. We have seen also that those micro-organisms which have been chemically studied produce, like the higher animals, perfectly definite chemical changes. There is in this respect, therefore, no essential difference between a mass of yeast, a populous town, a herd of cattle, and a colony of snakes; each produces its own peculiar chemical changes in the food it consumes.

The position of micro-organisms in nature is only just beginning to be appreciated. Their study, both from chemical and biological points of view, is however of the highest importance to the welfare of mankind; and I venture to predict that whilst there is no danger of their being spoiled by petting, or by their welfare being made the special care of sentimentalists, these lowly organisms will receive much more attention in the future than they have done in the past. Their study leads the inquirer right into those functions of life which are still shrouded in obscurity, and it is to be hoped that these investigations will not be retarded by mischievous legislation.

XXIV.—*Toughened Filter-papers.*

By E. E. H. FRANCIS, Government Chemist, British Guiana.

IN attempting to prepare pyroxylin filters, the writer found that paper was remarkably toughened by the action of nitric acid, the product being pervious to liquids, and quite different from parchment-paper made with sulphuric acid. Simple immersion in, or mere moistening with nitric acid of density 1.42, and subsequent washing with water, are sufficient to produce the effect, and no particular precautions are necessary.

The toughened paper can be used like the ordinary kind, filtration being but little retarded, whilst the closeness of its texture and the absence of all pin holes render its action very efficient. It can be washed and rubbed without damage like a piece of linen, and is therefore likely to prove useful for the collection of substances that have to be removed from the filter whilst wet. Comparative trials were made of the strength of wet Swedish paper before and after being toughened. A strip of each 25 mm. wide was made into a loop, and the ends held in a vertical clamp; through the loop was passed a glass rod 5 mm. in diameter, to which by strings at each end a

scale-pan was attached. Ordinary filter-paper broke with a weight that varied from 100 to 150 grams, whilst the toughened paper bore a weight of about 1·5 kilos. before it gave way, and is therefore more than ten times as strong as the other. In consequence of its great tenacity the toughened paper can be used in ordinary funnels with the vacuum pump. Several trials were made, and it was found to bear the greatest pressure produced by the pump employed (a common exhausting syringe), whilst a single stroke of the piston broke the ordinary paper. The treatment with nitric acid producing but little change in texture, the toughened paper fits sufficiently closely to the funnel to prevent undue access of air, and is therefore not open to the objection made against the parchment filters recommended by C. Tichborne (*Pharm. J. Trans.*, 1871, 881). An admirable way of preparing filters for the pump is to dip only the apex of the folded paper into nitric acid, and then wash with water; the weak part is thus effectually toughened, whilst the rest remains unaltered.

The paper contracts in size under the treatment, and the ash is diminished. Thus circles 11·5 cm. in diameter became reduced to 10·4 cm., or about one-tenth, whilst the ash was reduced from 0·0026 to 0·0011 gram. The toughened paper contains no nitrogen. To determine this point, a portion was gently heated in a test-tube with strong sulphuric acid, by which it was almost immediately decomposed and carbonised. Water was added and the mixture filtered, a clear white filtrate being obtained. On this, when cold, solution of ferrous sulphate was carefully poured, but no coloration was produced, nor were brown fumes or a nitrous odour perceived at any stage of the testing. On the other hand, similar paper that had been converted into pyroxylin with the same nitric acid mixed with an equal bulk of oil of vitriol, dissolved in warm sulphuric acid without blackening, abundance of brown fumes being evolved, and the solution after dilution reacted strongly with ferrous sulphate. Moreover, the toughened paper gave no evidence of containing nitrogen by Lassaigne's test, and it burns like ordinary paper, and not at all like pyroxylin.

Subjected to the action of nitric acid of the strength specified, paper undergoes no increase in weight, as is the case when pyroxylin is formed, but, on the contrary, there is a slight decrease. Thus, a circle of Swedish paper 11·5 cm. in diameter weighed 0·6795 gram before treatment with nitric acid, and afterwards it weighed only 0·6749 gram, showing a loss of 0·68 per cent.

The effect of nitric acid on paper does not appear to have been studied very completely. Gmelin states (*Handbook*, 15, 135), apparently on his own authority, that "cotton, linen, or paper immersed for two or three minutes in nitric acid of sp. gr. 1·5 acquires the

texture of parchment, and is rendered impervious to light and water because it becomes covered with a film of xyloidin," and further, that "paper immersed in cold strong nitric acid swells up to a jelly, which gives a blue colour with iodine on isolated spots, and therefore contains starch;" and, on the authority of Mitscherlich, that "Swedish paper is not at all decomposed by immersion in cold nitric acid of sp. gr. 1.2, and but slightly in the acid heated to 100°." No further information than this has been found by the writer.

XXV.—*A Quick Method for the Estimation of Phosphoric Acid in Fertilisers.*

By J. S. WELLS.

As I have had to make a great many analyses of fertilisers, and the ammonium molybdate method is so long and tedious, I was led to seek a process which would be more expeditious and at the same time give equally good results. The method to be generally applicable must be one in which the presence of iron and alumina does not interfere, as these substances are very often present in fertilisers. While examining the different volumetric methods, the idea occurred to me that Joule's citric acid process might be so modified as to be used gravimetrically; in this way I have obtained results corresponding very closely with those obtained by means of ammonium molybdate.

The modified process is as follows:—Two solutions are made up, one, which we will call "A," consisting of citric acid 900 grams, ammonia (sp. gr. 0.92) 1400 c.c., and water 500 c.c. The second, or solution "B," is simply a strong solution of magnesium citrate, prepared by dissolving carbonate of magnesia in citric acid.

Total Phosphoric Acid.—1 gram of the fertiliser is taken and fused with a mixture of 3—4 grams of sodic carbonate and 3—4 grams of sodic nitrate; the product is dissolved in nitric acid, and any insoluble residue removed by filtration. If the fusion has not been continued too long, any silica contained in the fertiliser will remain insoluble, and will be left in the residue.

To the filtrate, enough of the solution "A" is added, usually about 10 c.c., so that on making the mixture alkaline with ammonia no precipitate is formed, except possibly a slight one of silica.

It is now allowed to remain for about half an hour, and if any silica has separated it is filtered, and to the filtered solution suffi-

cient of solution "B" is added to precipitate the phosphoric acid; it is stirred well and allowed to stand for some time. The precipitate obtained is washed and weighed in the usual way. The result gives the total phosphoric acid present.

Soluble Phosphoric Acid.—In order to obtain the soluble phosphoric acid, another gram of the phosphate is taken and treated with water in the usual way.

To the solution thus obtained sufficient of "A" is added to prevent precipitation by the ammonia, which is now added in excess, and then enough of "B" to precipitate the phosphoric acid. The precipitate is washed and weighed as usual, and gives the amount of soluble phosphoric acid.

Reverted Phosphoric Acid.—The residue left after the extraction of the acid soluble in water is then treated with a solution of ammonium citrate in the usual manner to extract the reverted acid.

The solution thus obtained cannot be used to determine the amount of reverted phosphoric acid, as I found that the results obtained by precipitating the phosphoric acid contained in it are untrustworthy; sometimes the acid is completely precipitated, and at other times only partly. I think the reason of this is the very large quantity of ammonium citrate present in the solution.

Finding that the acid could not be readily determined in this solution, I have obtained it by difference, *i.e.*, the sum of the percentages of the soluble and insoluble acid is subtracted from the percentage of the total phosphoric acid, and the difference is of course the reverted acid.

Insoluble Phosphoric Acid.—The residue left after extracting the reverted acid now contains only the insoluble acid. It is fused with sodium carbonate and nitrate, and the phosphoric acid determined in exactly the same way as the total phosphoric acid was.

My first experiments were made on a solution containing a known amount of phosphoric acid. This solution was made up of sodium phosphate, calcium chloride, and ammonium iron alum, so as to contain P_2O_5 19.83 per cent., CaO 25 per cent., Fe_2O_3 3 per cent. Equal portions of this solution were taken for each determination, and the results obtained were as follows:—

No. 1..	Time.	Per cent. found.	Theory.
2..	2 hours	19.62 per cent.	19.83 per cent.
" 3..	"	19.77	" "
" 4..	18 "	19.84	" "
" 5..	"	19.84	" "
" 6..	"	19.74	" "
" 6..	"	20.06	" "

Numbers 1 and 2 show that the precipitation was nearly complete at the end of two hours. In No. 5 a solution of sodium silicate was added, then solution "A," and then ammonia to alkaline reaction. After standing one hour the separated silica was filtered off, and the phosphoric acid precipitated by solution "B." To No. 6 sodium silicate was added, and the phosphoric acid precipitated without previous removal of silica. After weighing, the precipitate was boiled with strong nitric acid, the insoluble residue of silica filtered and weighed, and the weight deducted from that of the first precipitate.

The results obtained being so satisfactory, I then tried the method on several fertilisers, with the following results:—

	Ammonium citrate method.	Ammonium molybdate method.
No. 1.	4.23 per cent.	4.23 per cent.
„ 2.	18.36 „	18.18 „
„ 3.	3.42 „	3.64 „
„ 4.	14.01 „	13.92 „

In making an analysis, care must be taken not to mistake a possible precipitate of magnesian phosphate for one of silica, when the alkaline solution is allowed to stand so as to separate silica. The difference in the appearance of the two will, however, enable one to easily distinguish between them. If silica and magnesia should happen to occur together in the same phosphate, it would be best to remove the former in the usual way by evaporating the acid solution to dryness.

XXVI.—*The Oxides of Nitrogen.*

By W. RAMSAY and J. TUDOR CUNDALL.

THE researches of chemists on the methods of production and formula of nitrogen trioxide are somewhat difficult to reconcile with each other. It is commonly believed that the indigo-blue or green liquid produced by the action of arsenious anhydride on nitric acid has the formula N_2O_3 ; and that it is capable of direct union with oxygen, forming nitric peroxide. Early in 1884 an attempt was made in this laboratory to convert this green liquid into a red one by passing a current of oxygen through the green liquid kept in a freezing mixture; but the change of colour was so slow, and the excess of oxygen used was apparently so large, that there was some doubt as to the

possibility of direct union. And on referring to the literature of the subject there appeared sufficient grounds for a new investigation. The colour of nitrogen tetroxide is markedly red, and that of the product of the action of arsenious anhydride on nitric acid of so deep a blue, that it appeared probable that a mixture of the trioxide and tetroxide of nitrogen would be of some intermediate tint; yet analyses of the blue liquid always point to its being a mixture of both trioxide and tetroxide. Hasenbach (*J. pr. Chem.* [2], 4, 1) states that nitric oxide and peroxide unite to form the trioxide when passed through a red-hot tube; and he also states that the trioxide prepared in this way can be reconverted into nitric peroxide by passing a current of oxygen through it when kept in a freezing mixture.

It has been remarked by J. Moser (*Pogg. Ann.* [2], 2, 139) that the absorption-spectra of gaseous trioxide and tetroxide are identical; this would imply at least partial dissociation according to the equation: $\text{N}_2\text{O}_3 = \text{NO}_2 + \text{NO}$.

It is hardly to be expected that a liquid of a deep blue colour would yield a gas having properties optically identical with the gas of a red liquid, and a dispute has arisen on that point (*Berl. Ber.*, 11, 1229—1641; 12, 357 and 2188) between Lunge and Witt. Whilst Witt maintains that the product of the action of arsenious oxide or starch on nitric acid consists essentially of peroxide, any nitrous anhydride fumes dissociating completely on passing into gas, Lunge has endeavoured to show that the gas absorbed by sulphuric acid consists wholly of N_2O_3 . His argument is that if dissociation were to take place the nitric oxide would escape absorption; Witt, however, replies that sulphuric acid containing nitric acid is capable of absorbing nitric oxide.

We hope that this research may be considered as reconciling these contradictory statements.

The substance which served as a starting-point for our investigations was prepared by the action of nitric acid on arsenious oxide. Sometimes pure strong nitric acid (density 1.5) was used, and in some cases strong sulphuric acid was added to the mixture before applying heat.

The gas was first passed through a U-tube containing arsenious oxide to react with any nitric acid that might have been carried over, and it was then dried. The only suitable drying agent was found to be phosphoric pentoxide, as the gas dissolved in sulphuric acid (reacting with it), and it also reacted with calcium chloride forming nitrosyl chloride.

The gas after passing through U-tubes containing phosphorus pentoxide was led into a bulb with two necks surrounded with a freezing mixture of ice and hydrochloric acid. To complete the

apparatus, another drying tube was added to prevent moisture diffusing back. Joints as far as possible had to be sealed; where this was impossible, corks were used, india-rubber being quite inadmissible. The liquid was then put into small weighed bulbs with long stalks, the bulbs holding about 0.75 c.c. The stalks were afterwards sealed and re-weighed, thus giving the weight of liquid taken.

The first method of analysis which we adopted was as follows:—One of the weighed bulbs of oxide was placed in a well-stoppered bottle holding about 700 c.c., together with 25 c.c. of normal standard caustic soda (in case of very large bulbs 50 c.c. of soda were taken); some water was added to prevent heating, and the bulb was broken by shaking the bottle. The bottle was then well shaken until all the oxide had combined with the soda; and the uncombined soda was titrated with standard sulphuric acid, phenolphthalein being used as an indicator.

Method of Calculation.

Let x = number of c.c. of standard soda
and y = " " acid
∴ $x - y$ = " soda neutralised by the nitrogen oxide.
1 c.c. of standard soda contains 0.04013 gram of NaHO.
∴ $(x - y) 0.04013$ = weight of NaHO neutralised by the nitrogen oxide.

But 1 equivalent of NaHO = 1 equivalent of nitrogen, whether as nitrous or nitric acid.

Hence $\frac{(x - y) 0.04013 \times 14}{40}$ = weight of nitrogen in 3 grams of oxide (the weight taken).

∴ Percentage of nitrogen in oxide = $\frac{(x - y) 0.04013 \times 14 \times 100}{40 \times 2}$

and subtracting this number from 100 gives the percentage of oxygen.

In the first batch of bulbs, the liquid was of indigo-green colour. Bulb 1 contained 0.7627 gram of liquid, and was broken into 25 c.c. of soda; calculating as above, this gives the result 30.4 per cent. of nitrogen and 69.6 per cent. of oxygen. Bulbs 2 and 3 gave the same result, which is therefore the mean of the batch, and is precisely the percentage in nitrogen peroxide (N_2O_4). Tabulating this and subsequent results gives the following table:—

Batch.	Bulb.	Nitrogen per cent.	Oxygen per cent.	Mean per cent. of N.	Colour.	Method of formation.
I....	1	30·4	69·6	—	indigo-	From As_2O_3 , HNO_3 , and H_2SO_4 .
	2	30·4	69·6	30·4	green	
	3	30·4	69·6	—	—	
II....	1	28·1	71·9	28·94	olive-	Similar to I.
	2	29·79	70·21	—	green	
III....	1	29·6	70·4	28·65	red	Similar to I.
	2	27·7	72·3	—	—	
IV....	1	31·93	68·07	31·56	indigo-	By passing NO over batch III.
	2	31·20	68·80	—	blue	
V....	1	31·2	68·8	—	—	Similar to I.
	2	29·98	70·02	29·82	red	
	3	28·3	71·7	—	—	
VI....	1	30·4	69·6	30·5	indigo-	By passing NO over batch V.
	2	29·7	70·3	—	blue	
VII....	1	28·6	71·4	28·5	green	By passing O over batch VI.
	2	28·4	71·6	—	—	

The inferences that may be drawn from these figures are, firstly, that the method of estimation gives the nitrogen too low, probably on account of nitric oxide being formed and not being acted on by the soda. Secondly, that the blue liquid contains a far smaller percentage of nitrogen, if it be N_2O_3 , than it should proportionally to the red liquid which is presumably N_2O_4 . Thirdly, that passing nitric oxide over the red liquid gives a blue liquid in which the percentage of nitrogen is increased, but only to a limited extent. And, lastly, that passing oxygen in the same way reduces the percentage of nitrogen.

After this plan had been tried, some confirmatory methods were sought, but for some time without success. The first of these was to estimate the nitrous acid in the neutralised solutions of the previous process by means of standard potassium permanganate, but this was found unsatisfactory on account of the inconvenient and tedious time reactions which take place. Then a method involving the use of iodide of potassium and standard sodium thiosulphate was tried in the same manner, but failed for a similar reason.

An entirely different principle was now tried, depending on the fact that when nitrous acid is warmed with hypobromite of soda it gives off its nitrogen; in this case, however, the results were found to be so untrustworthy as to be useless. This last remark also applies to the fourth unsuccessful method, which consisted in combining the oxide

with ammonium hydrate; it was thought that ammonium nitrite would be formed and that, on boiling, this would decompose into nitrogen and water. It was found, however, that the results obtained in this reaction were not quantitative. Advantage was then taken of the fact that when nitrogen trioxide or tetroxide is dissolved in sulphuric acid, and the solution is shaken with mercury, all the trioxide or tetroxide is evolved as nitric oxide. This reaction was made use of in the following way:—

A thickish glass tube, about 90 cm. long and 2 cm. in cross section, was graduated into mm., filled with mercury, and inverted in a trough. One of the bulbs was then slipped in and the height of the mercury measured both with a cathetometer and on the tube; this gave the barometric pressure. The bulb was then broken by shaking (a piece of glass rod being inserted to aid this process), and when all the liquid had evaporated the height of the mercury was measured in the same way. (This reading was taken for a purpose to be considered hereafter.) It may be well to mention here that the mercury was not appreciably attacked by the gas.* Then about 10—20 c.c. of strong sulphuric acid was passed up the tube by means of a bent pipette, and the tube was shaken to make the gas dissolve; nitric oxide was immediately evolved, and to complete the action the tube was shaken lengthways to break up the mercury and bring it in thorough contact with the sulphuric acid. The tube was allowed to stand until it had acquired the temperature of the air; this was then observed, and the height of the mercury read as before. The volume occupied by the gas was found by emptying the tube, inverting it, and filling it up to the read height with water from a burette, allowance of course being made for the volume of the piece of glass used to break the bulb.

The volume of the nitric oxide was corrected for temperature, and for the pressure diminished by the length of the column of mercury. The pressure exerted by the column of sulphuric acid was calculated and added.

The percentage of nitrogen in that volume, and hence in the weight of liquid taken, was calculated in the usual way. The following table gives the results of the analyses:—

* Naumann states that the peroxide slowly attacks mercury. In ascertaining the vapour-density of the peroxide at various temperatures and pressures, he allowed for a slow contraction produced by this action on mercury. It is probable that the care which was taken in drying the product we used was the cause of the mercury remaining unattacked: certainly no contraction was observed, even after some hours' standing, although the surface of the mercury became at once somewhat tarnished.

Batch.	Bulb.	Percent- age of N.	Percent- age of O.	Mean per cent. of N.	Remarks.
A	1	29·9	70·1	—	Colour greenish, made from As_2O_3 , HNO_3 , and H_2SO_4 .
	2	30·5	69·5	30·2	
B	1	29·67	70·33	29·8	Colour olive-green. Made similarly to A.
	2	29·93	7·07	—	
C	1	25·59	70·41	29·69	Colour red. Made similarly to A.
	2	29·79	70·21	—	
D	1	31·47	68·53	—	Colour indigo-blue. Made by bubbling NO into batch C. Bulb 1 taken half way, 2 three quarters, and 3 at end of process.
	2	31·73	68·27	—	
	3	32·50	67·50	—	
E	1	28·82	71·18	29·06	Colour red. Made similarly to A.
	2	29·31	70·69	—	
F	1	32·81	67·19	32·44	Colour indigo-blue. Made by mixing the vapour of E with excess of NO, and condensing product at -20° to -25°C . Liquid very volatile.
	2	32·50	67·50		
	3	32·70	67·30		
	4	32·80	67·20		
	5	31·75	68·25		
	6	31·60	68·40		
	7	31·97	68·03		
	8	32·97	67·03		
	9	32·88	67·12		

In batch A only a small proportion of sulphuric acid was used, hence the greenish colour, which in batch B we find is turning more olive-green, *i.e.*, is more nearly peroxide, more sulphuric acid having been used.

With batches C and E excess of sulphuric acid was employed, and pure peroxide was produced. With batch D the NO was bubbled through the liquid; and it is noticeable that the end percentage is about the same as the mean percentage in batch F, when a greater excess of NO was used, and the oxides were mixed in the gaseous state. From the reading taken before the sulphuric acid was passed up, the vapour-densities at the particular temperatures and pressures were calculated for batch F, and this leads to an important result.

The volumes being read and corrected, and their weights being known, the vapour-densities were easily calculated. They are given in the subjoined table:—

Bulb.	Volume.	Weight taken.	Temperature.	Pressure.	Derived V.D.
1	125.0 c.c.	0.1590 grm.	19.5° C.	342.8 mm.	33.73
2	125.5 "	0.1679 "	13.2 "	356.7 "	33.36
3	143.2 "	0.1625 "	17.4 "	298.5 "	34.31
4	153.0 "	0.1990 "	15.7 "	331.8 "	35.18
5	142.0 "	0.2186 "	10.9 "	396.0 "	34.22
6	144.5 "	0.2280 "	10.0 "	403.5 "	34.39
7	147.0 "	0.2400 "	9.8 "	415.3 "	34.55
8	164.5 "	0.3242 "	10.5 "	481.5 "	36.05
9	179.0 "	0.3887 "	9.8 "	521.5 "	36.90

From the analyses (here we are only dealing with batch F) the mean percentage of nitrogen was found to be 32.44 per cent. Let us call this percentage a . Then percentage of oxygen = $100 - a$.

Composition by theory, N_2O_4 . N p. c. = 30.43. O p. c. = 69.57.
 N_2O_3 . N p. c. = 36.84. O „ = 63.16.

But the liquid obviously consists of a mixture of N_2O_3 and N_2O_4 .

Let $x = N_2O_4$ per cent.; then $100 - x = N_2O_3$ per cent.

Then $30.43x + 36.84(100 - x) = 3244$.

whence $n = 68.64$.

Therefore the percentage of N_2O_3 in the mixture = 31.3, and $N_2O_4 = 68.7$.

It seems highly probable that the nitrogen trioxide dissociates when it changes into gas, $N_2O_3 = NO + NO_2$, or more correctly, $N_2O_3 = NO +$ a varying mixture of NO_2 and N_2O_4 , according to temperature and pressure.

Now, as it is doubtful to what extent this dissociation takes place, it was necessary to find what the vapour-density would be if the gas were wholly dissociated into NO and N_2O_4 . But N_2O_4 is itself a dissociable gas, giving NO_2 in varying quantities, at different temperatures and pressures. The extent of this dissociation has been investigated by Playfair and Wanklyn, by Troost, and by Naumann, and from their numbers a formula representing the extent of dissociation has been calculated by J. W. Gibbs (*Amer. Jour. Sci.*, 18, 1879).

This equation is—

$$\text{Log } \frac{15.89(D - 1.589)}{(3.178 - D)} = \frac{3118.6}{t_c + 273} + \text{log } p \cdot 12.451,$$

t_c denoting the temperature on the centigrade scale. The numbers 3.178 and 1.589 represent the theoretical densities of N_2O_4 and NO_2 respectively, as compared with air. The two other constants were

determined by the experiments of Deville and Troost. Another difficulty arises from the presence of NO, owing to the decomposition of the N_2O_3 . This nitric oxide occupies volume and reduces pressure as far as the NO_2 and N_2O_4 are concerned. As in air at 760 mm., the oxygen is exposed to a partial pressure (for it occupies one-fifth of the total volume, and is spread out through the whole volume), so the presence of nitric oxide reduces the pressure on the other constituents of the gaseous mixture. Hence it is necessary to calculate the weight and volume of the NO present, on the supposition that all the N_2O_3 has been decomposed into NO and $(NO_2 + N_2O_4)$. This amount was accordingly calculated; analysis and the previous calculation showing the substance to contain 31.3 per cent. of nitrogen trioxide. This nitrogen trioxide, if we may regard it as dissociated, would give the following numbers: 76 parts by weight of nitrogen trioxide would dissociate into 46 parts of $(N_2O_4 + NO_2)$ and 30 parts of nitric oxide. Therefore, by a very simple calculation, we find that the above-mentioned 31.3 per cent. of trioxide would give, by dissociation, 18.967 per cent. of tetroxide. Adding this 18.967 per cent. to the 68.7 per cent. already present, we have a total of 87.67 per cent. of $(N_2O_4$ and $NO_2)$. Subtracting this number from 100 gives 12.33 per cent. by weight of NO. Now, applying this to the result with bulb 1, we have as the weight of substance taken 0.1590 gram, containing 12.33 per cent. of NO, or 0.019605 gram; this weight occupies at standard temperature and pressure, a volume of 14.59 c.c., which, being corrected to the observed temperature (195° C.) and pressure (342 mm.), gives a volume of 34.74 c.c. But the total volume at the observed temperature and pressure is 125 c.c. Subtracting from that the volume of NO (34.74 c.c.), we arrive at the volume of the $(NO_2 + N_2O_4) = 90.26$ c.c. Therefore the pressure is diminished (as in the before cited case of oxygen in air) in the proportion of 125 : 90.26. And calculating from this the actual pressure to which the $(NO_2 + N_2O_4)$ is subjected, we find that the observed pressure is reduced from 342.0 mm. to 247.0 mm.

Now, the theoretical density of $(NO_2 + N_2O_4)$ at 19.5° and 247.0 may be calculated by means of J. W. Gibbs's formula, where if we set—

$$\Delta \text{ (a constant given in his table)} = \frac{D}{D_1}. \text{ Then}$$

$$L = \log \frac{1000D_1(D - D_1)}{(2D_1 - D)^2} = \log \frac{1000(\Delta - 1)}{(2 - \Delta)^2},$$

we have for peroxide of nitrogen $(NO_2 + N_2O_4)$.

$$L \text{ (the V.D. compared with air)} = \frac{3118.6}{t_c + 273} + \log p - 9.451.$$

On taking the corresponding value of Δ in Gibbs's table, we find that the vapour-density compared with air of the substance in this case is 2.5583, or compared with hydrogen 36.93.

Having now the density of our two components, it is easy to calculate the density of the mixture of 87.67 parts of ($\text{NO}_2 + \text{N}_2\text{O}_4$) of density 36.93 with 12.33 parts of NO of density 15.0.

$$D = \frac{(87.67 \times 36.93) + (12.33 \times 15)}{100};$$

Whence $D = 34.225$; whereas the found density was 33.73, a sufficiently close approximation. Applying this calculation to all the vapour-densities we get the following table:—

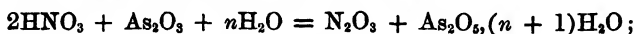
Bulb.	1.	2.	3.	4.	5.
t° (observed)	19.5°	13.2°	17.4°	15.7°	10.9°
p	342.0	356.7	298.5	331.8	396.0
Weight in grams	0.1590	0.1679	0.1625	0.1990	0.2186
Vol. in c.c. = A	125.0	125.5	143.2	153.0	142.0
Corr. vol. of NO = B	34.74	34.44	39.96	44.24	40.03
A - B	90.26	91.09	103.24	108.76	101.96
Corr. press.	247.0	258.9	215.2	235.8	284.37
L	3.604	3.859	3.732	3.872	3.968
D_1 (Theor. V.D. of $\text{NO}_2 + \text{N}_2\text{O}_4$) ..	36.93	38.76	37.89	38.92	39.68
D_2 (Theor. V.D. of subs.)	34.22	35.83	34.07	35.95	36.63
Found V.D. of substance	33.73	33.36	34.31	35.18	34.22

Bulb.	6.	7.	8.	9.
t° (observed)	10.0°	9.8°	10.5°	9.8°
p	403.5	415.3	481.5	521.5
Weight in grams	0.2280	0.2400	0.3242	0.3887
Vol. in c.c. = A	144.5	147.0	164.5	179.0
Corr. vol. of NO = B	40.85	41.75	48.76	58.86
A - B	103.65	105.25	115.74	120.14
Corr. press.	289.43	297.35	338.78	350.01
L	4.030	4.050	4.079	4.121
D_1 (Theor. V.D. of $\text{NO}_2 + \text{N}_2\text{O}_4$) ..	39.86	39.95	40.117	40.37
D_2 (Theor. V.D. of subs.)	36.80	36.88	37.02	37.24
Found V.D. of substance	34.39	34.55	36.06	36.9

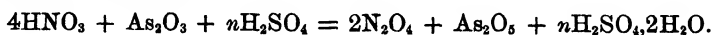
Thus it is plain that the N_2O_3 prepared by us does not exist in the state of gas; but, if cooled, it condenses to a liquid more or less mixed with ($\text{N}_2\text{O}_4 + \text{NO}_2$), in which the highest percentage of N_2O_3 found is only about 30 at -25°C ., but probably would increase at lower temperatures.

To recapitulate, the facts worthy of note are—

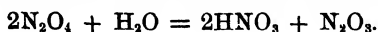
Firstly, that arsenious oxide when heated with nitric acid gives a liquid containing N_2O_3 according to the equation—



but that when the water given off in this reaction is absorbed by sulphuric acid no N_2O_3 is formed, but a red liquid consisting of $(N_2O_4 + NO_2)$, thus:—



We may also suppose this to be the normal reaction, and assume that the peroxide is subsequently decomposed by water, thus:—



If ordinary nitric acid be used, there is complete dissociation of the resulting N_2O_3 immediately on its passage into the gaseous state; and on cooling with a freezing mixture a portion of the peroxide condenses as such, while a portion combines with the nitric oxide present to form trioxide.

Secondly, the passage of NO through this red liquid seems merely to produce N_2O_3 to a certain extent, depending on the temperature; and this amount is not increased by great excess of NO.

Thirdly, the passage of oxygen into the blue liquid converts it into $(N_2O_4 + NO_2)$, but this reaction is a very slow one. It is indeed doubtful if the reaction takes place with liquid trioxide.

Fourthly, the presence or absence of moisture does not appear to influence the combination. To settle this point, on January 10th, 1885, a large bulb of oxygen very carefully dried was sealed up with phosphoric pentoxide, inside a larger bulb of very carefully dried nitric oxide, also in contact with a large amount of phosphoric pentoxide. On January 15th, the inside bulb in the first apparatus was broken, and a red colour appeared. On February 9th another was broken, and the red colour again appeared, showing that combination had taken place. On February 16th a third was broken with the same effect.

Lastly, nitrogen trioxide does not exist in the state of gas, and probably not as a pure liquid, except perhaps at very low temperatures. It is probable that dissociation occurs even in the liquid state. It is well known that the liquid peroxide, when cooled, becomes colourless, and when heated, of a brown-red colour. A very thick piece of barometer tubing filled with a dark-blue specimen, presumably rich in trioxide, was heated in boiling water; and its colour changed to the indefinite mixed shade of red and green. No evolution of gas from the liquid was observable, and, on cooling, the whole of the liquid changed to a blue colour, and not the surface merely; the latter might have been expected if the liquid had given off nitric oxide, which

would naturally fill the upper half of the tube, and react gradually with the peroxide, attacking the top layers first. It is, however, conceivable that the deepening in intensity of colour which the peroxide undergoes on heating may have produced the change from blue to the mixed tint.

[ADDENDUM, February 28th.—In the discussion on this paper, Dr. Armstrong stated that, in his opinion, nitrous acid is *the* product of the action of arsenious oxide on nitric acid, and that the reactions of more or less concentrated acid can be explained on this assumption by the following equations:— $3\text{HNO}_2 = 2\text{NO} + \text{HNO}_3 + \text{H}_2\text{O}$: but in presence of nitric acid, $\text{HNO}_2 + \text{HNO}_3 = \text{N}_2\text{O}_4 + \text{H}_2\text{O}$. Against this view, the authors have nothing to urge; but it appears to them that it is quite as legitimate to state that nitric peroxide is *the* product, and that it undergoes reactions as follows:—

1. If water is absent, (*i.e.*, removed from the sphere of action by a dehydrating agent) the peroxide distils over as such.
2. If water is present, $2\text{N}_2\text{O}_4 + \text{H}_2\text{O} = \text{N}_2\text{O}_3 + 2\text{HNO}_3$; and the mixture of gases resulting from the volatilisation of the N_2O_3 pass away.
3. With less water, these products are mixed with the original peroxide.

As regards the formation of nitrosyl sulphate, the authors have recently prepared it in large quantity by what they consider, after many trials, to be by far the simplest method, *viz.*, to add to cooled oil of vitriol in which some crystals of pyrosulphuric acid have been dissolved, liquid nitric peroxide, until the liquid, at first viscous, becomes mobile. At this stage, an abundant crop of crystals separates out, and the supernatant liquid consists largely of nitric acid. They would not, however, be understood to imply that by passing nitric oxide into a mixture of nitric and sulphuric acids, nitrosyl sulphate is not produced.

In conclusion, the authors wish to state definitely that the nitric oxide passed over the tetroxide, converting it into the blue liquid which they believe to be largely trioxide, cannot have contained enough water to cause the reaction $2\text{N}_2\text{O}_4 + \text{H}_2\text{O} = \text{N}_2\text{O}_3 + 2\text{HNO}_3$ to take place; for the nitric oxide was dried by slow passage first through strong sulphuric acid, then through three long U tubes filled with phosphoric anhydride, and, finally, was mixed with gaseous peroxide dried in a similar manner; the mixture obtained in this way condensed, forming the blue liquid. This experiment was undertaken

with the express object of ascertaining whether water was the determining cause of the combination.

It may be that absolute freedom from water is not attainable even with these precautions; but the minute trace of water, if present, would, in these experiments, play a part analogous to that which Mr. Harold Dixon has recently shown it to perform in determining the combination of carbon monoxide with oxygen.]

XXVII.—*Note on Methylene Chloriodide.*

By J. SAKURAI, Professor of Chemistry, University of Tokio, Japan.

SOME time ago I had the honour of communicating to this Society the results of my experiments on a new series of organo-metallic compounds containing the bivalent radicle (CH_2).*

One of the last described was mono-mercuric methylene chloriodide, CH_2HgClI ; and in order to decide whether the iodine-atom in this compound was united to the methylene-group or to the mercury, the action of iodine upon it was tried (Trans., 1882, p. 360): it was stated that an oily liquid was produced together with mercuric iodide. This oily liquid was further shown to be methylene chloriodide, although the analytical results then obtained were not very satisfactory on account of the very small quantity of the liquid at my disposal.

I have lately prepared methylene chloriodide from an entirely different source in a state of purity and in a somewhat larger quantity than on the previous occasion. A comparison of the properties of this compound obtained from two different sources has perfectly satisfied me as to the correctness of my former conclusions.

Iodine monochloride was allowed to act on an excess of methylene iodide at the ordinary temperature. There was an immediate action with evolution of heat and separation of much iodine. Care was taken to add the monochloride little by little and with constant shaking so as to avoid any rise of temperature as far as possible. After some hours, the contents of the flask in which the reaction was carried on were distilled: a small portion came over a little above 40° , and the

* Trans., 1882, p. 360. In this paper, on p. 362, there are two misprints, which I take this opportunity of correcting. In line 6 from the top, "mercuric chloride" should read "mercuric chloriodide," whilst in line 17, the boiling point of the oily liquid, methylene chloriodide, is given as 129° , whereas it should be 109° .

temperature gradually rose to about 130° , when it was found necessary to stop the distillation on account of the large quantity of iodine-vapour coming over.

The distillate, which was freed from iodine by means of dilute potash solution, was carefully washed and dried, and then subjected to several fractional distillations. A colourless liquid boiling between 40° and 45° formed part of the distillate, but the main portion consisted of a somewhat heavy oil boiling between 107° and 110° ; on again fractionating, a liquid boiling constantly at $109-109.5^{\circ}$ (bar. pressure = 760.4) was finally obtained. When pure, it is a colourless oil with a slight tinge of yellow, but on exposure to light it soon becomes slightly reddish. Two density determinations were made with the following results:—

$$d_{11^{\circ}}^{11^{\circ}} = 2.447 \qquad d_{14.5^{\circ}}^{14.5^{\circ}} = 2.444.$$

Ordinary tests soon showed the presence of both chlorine and iodine in the compound, the amount of which was determined by Carius' method:—

Weight of liquid taken.	=	0.3952
„ mixed chloride and iodide of silver. .	=	0.8481
„ total chloride of silver	=	0.6426
Hence, loss on fusion in chlorine gas.	=	0.2055

Adopting the atomic weights $\text{Ag} = 108$, $\text{Cl} = 35.5$, $\text{I} = 127$, these data lead to 72.17 per cent. iodine and 20.05 per cent. chlorine. The numbers calculated for $\text{CH}_2\text{I}\text{Cl}$ are 71.95 per cent. iodine and 20.11 per cent. chlorine.

Its vapour-density was determined by Hofmann's method, and was found to be 88.14. Theory requires 88.24.

We may therefore safely conclude that the liquid under examination is methylene chloriodide, CH_2ClI . Let me again call attention to the fact that its boiling point is very nearly the mean of the boiling points of methylene chloride and iodide, and this property as well as its density, as found on the present occasion, agree well with what I formerly described.

From these observations, it is evident that the liquid I previously obtained by the action of iodine on the mercury compound is really methylene chloriodide; and this strongly confirms the view that the mercury compound is represented by the formula $\text{CH}_2\text{Cl.HgI}$, and not by $\text{CH}_2\text{I.HgCl}$.

It was stated above that a small portion of the distillate consisted of a colourless oil which boils between 40° and 45° . The halogen element in this liquid was found to be almost entirely chlorine, there

being only a very minute quantity of iodine present. This portion of the distillate consists then essentially of methylene chloride, which is almost an unavoidable bye-product in the formation of the chloriodide. The reaction between iodine monochloride and methylene iodide, under the conditions described, is therefore—



XXVIII.—*The Illuminating Power of Methane.*

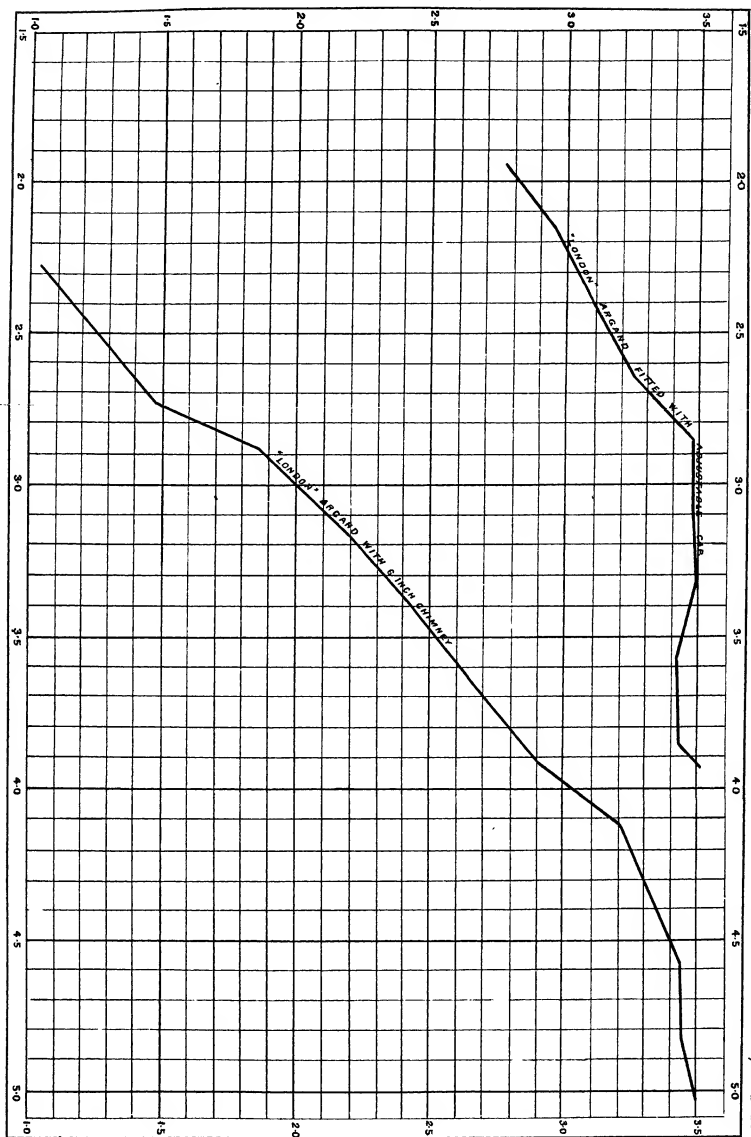
By LEWIS T. WRIGHT, Assoc. M.I.C.E.

It is generally understood that the methane (marsh-gas) flame is feebly luminous, but at present I am not acquainted with any published record of its illuminating power in terms of any standard. The recent description of an easy method of preparing pure methane by Gladstone and Tribe (*Chem. Soc. J.*, 45) tempted me to prepare sufficient quantities of this gas for the proper determination of its illuminating power. I find, however, that the apparatus described by them is not well adapted for the preparation of methane free from methyl iodide-vapour, for the first batches of gas I prepared with their apparatus were always found to be sensibly contaminated with this body, which made itself very evident on the combustion of the gas by irritating iodine-vapours in the products of combustion.

Instead of adopting special methods of purification, based upon other reactions of methyl iodide and involving complicated and cumbersome apparatus, it occurred to me that by a special disposition of apparatus Gladstone and Tribe's elegant method of preparation might be rendered complete in itself.

The vertical tube used by them as a scrubber is inefficient for the retention of the methyl iodide-vapour which escapes with each bubble of gas from the generating flask, for the copper-zinc in it soon loses the alcohol with which it has been moistened, and the impure gas is no longer "scrubbed," but simply passes through a column of dry copper-zinc. As it would not be convenient to keep the copper-zinc in the vertical tube always saturated with alcohol, I placed after the apparatus a series of three copper tubes, 12 inches long $1\frac{1}{2}$ inches diameter, in a horizontal position, fitted with corks bored centrally for glass tubes and so arranged as to admit of a slight rotation. These tubes were filled with copper-zinc and as much alcohol as they would hold in the horizontal position. These tubes are succeeded by one of

Standard Sperm Candles per Cubic Foot per hour.



Cubic Feet per hour, corrected to 30' in Bar. 60° F.

Harrison & Sons Ltd 5 Marine Lane N.C.

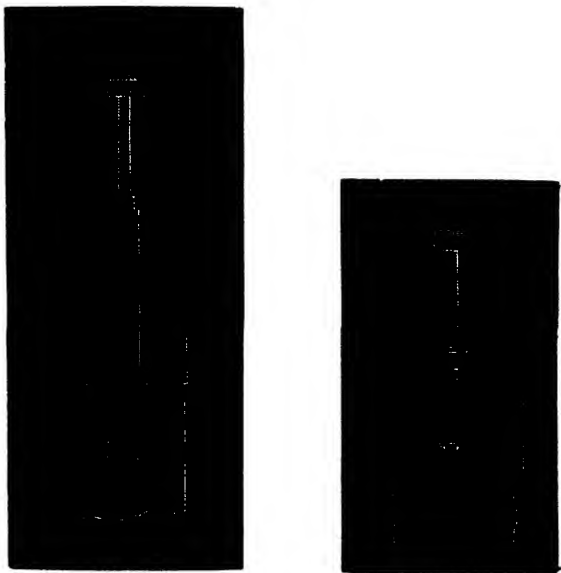
Journ. (Intern. Soc.) April 1885.

glass charged with glass beads and sulphuric acid to absorb the alcohol-vapour.

With this apparatus it is easy to prepare methane free from methyl iodide-vapour, but if I were arranging another apparatus I should dispense with the upright washing-tube altogether.

The methyl iodide used in these experiments was pure, boiling point $42-43^{\circ}$ (uncorr.), $= 2.2679$ at $d_{15}^{15^{\circ}}$.

The methane as prepared was collected in a small gas-holder made by Giroud of Paris, specially designed to replace a gasmeter in photometrical observations. Each division of the scale represents 5 c.c., and the total capacity of the holder is 5 litres. The outlet is directly connected with the burner of a good photometer provided with a Methven's standard burning 18-candle coal-gas which is known to give a uniform light of two candles. All the connections of the apparatus were arranged of small capacity in order to save loss of methane in the first displacement of air.



The burner used for the combustion of the methane was a London Argand with a 6-inch chimney, the top of which was provided with a metal cap capable of vertical adjustment by means of a fine-threaded screw. The object of this cap is the limitation of the air supply to the burner to the point at which the flame first begins to smoke. Some such arrangement is necessary with the Argand burner for low rates

of consumption, as otherwise the excessive air supply is prejudicial to the development of luminosity.

The importance of this point is indicated by the annexed tables showing the light afforded per cubic foot by $17\frac{1}{2}$ -candle coal-gas at various rates of consumption with and without the adjustable cap.

17.5 Candle Coal-gas burning in a London Argand Burner: 6-inch Chimney, without Adjustable Cap.

Rate of consumption. Cubic feet per hour.	Candles per cubic foot.
2.28	1.05
2.73	1.46
2.89	1.87
3.18	2.20
3.39	2.42
3.64	2.64
3.92	2.91
4.12	3.20
4.59	3.44
4.83	3.44
5.03	3.50

With Adjustable Cap.

1.95	2.77
2.16	2.96
2.39	3.09
2.65	3.25
2.86	3.47
3.05	3.47
3.32	3.49
3.93	3.51

Two samples of methane were tested photometrically with the following results:—

Rate of consumption per hour, corrected to 60° F. and 30" B. Cubic feet.	Candles observed.	Candles per cubic feet per hour calculated.
2.78	2.9	5.2
4.56	4.6	5.15

The luminous portions of methane flames obtained with Argand (flat flame and one-hole) burners were slightly yellow.

By sufficiently limiting the air supply of the Argand the methane flame smokes copiously. I hope to be able to extend these inquiries to other members of the paraffin series.

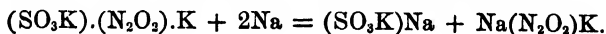
XXIX.—*Conversion of Pelouze's Nitrosulphates into Hyponitrites and Sulphites.*

By EDWARD DIVERS and TAMEMASA HAGA.

IN the first year of this century, Davy obtained indications of the existence of a potash salt of nitrous oxide or, in other words, of a potassium hyponitrite. Long afterwards, but still fifty years ago, Pelouze found these indications to be due to the formation of a potassium salt of nitrogen, sulphur, and oxygen—potassium nitrosulphate. It is now our fortune to be able to show that Davy, no less than Pelouze, was essentially right, inasmuch as we have succeeded in proving that Pelouze's salt is a hyponitrite compound—the *potassium hyponitrososulphate* or, more simply, *nitrososulphate*.*

Conceiving that nitrososulphates would have a constitution allied to that of a sulphate or thiosulphate, instead of the strange one given to them in which the nitric oxide stands as two additions to the radicles already carried by the sulphur of the sulphites, we have put our view to experimental test. The result of this has been that the current opinion as to the nature of these salts can no longer, we think, be upheld, unless it rests on other grounds than that of the want of a better.

The formation of a nitrososulphate is like that of a thiosulphate, with nitric oxide substituted for sulphur; and now we have found that, just as a thiosulphate when treated with sodium becomes sulphite again and sulphide, so a nitrososulphate becomes sulphite again and hyponitrite. We are therefore justified in expressing nitrososulphates and their decomposition in the following manner:—



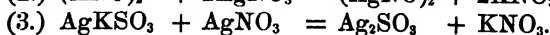
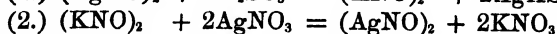
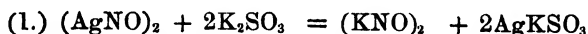
The experiment was carried out by treating pure potassium nitrososulphate in a concentrated solution of potassium hydroxide with sodium amalgam for many hours. This caused no sensible rise in temperature, very little evolution of gas, and a very slow decomposition of the salt. The potassium hydroxide, as it is known to do, protected the sodium from the action of the water, although it was also the means of greatly impeding the reduction of the nitrososulphate, because of the slight solubility of this salt in a strong solution of

* The latter slight modification of the old name, already in partial use, seems sufficient for all purposes. The salt might perhaps be called *sulphuric hyponitrite*; but it cannot, without confusion, be styled, as it has been, a *sulphonate*, since it contains metal outside the group SO_3K .

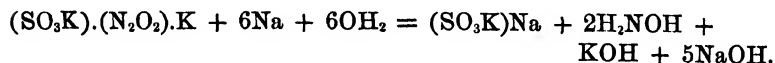
alkali. The hydroxide, however, could not have been dispensed with, as it was needed in order to preserve the hyponitrite when formed, and thus secure the presence of this in quantity. Together with the sulphite and hyponitrite, some hydroxylamine and a very little ammonia were generated. The hydroxylamine very soon ceased to increase in amount, probably in consequence of its being decomposed continuously by the strong alkali and yielding the ammonia.

When the action of the sodium was completed, the liquid was found to give a series of strikingly varied reactions with a solution of silver nitrate. At first there was a black precipitate of suboxide of silver produced by the hydroxylamine; then, this having been removed, brown precipitates of silver oxide appeared, dissolving in their mother-liquor on agitation; next came a bright yellow precipitate of silver hyponitrite; after this, silver oxide again, now no longer dissolving on shaking; and, lastly, a white precipitate of silver sulphite. The nature of the yellow and white precipitates was fully verified by appropriate tests.

The behaviour of the hyponitrite in this precipitation was exceptional, in that its silver salt took so long to appear. Some experiments with silver hyponitrite and potassium sulphite showed us the reason of this. Silver hyponitrite dissolves freely, like other silver salts, in potassium sulphite solution, and if silver nitrate is added to this solution when saturated, silver hyponitrite is reprecipitated before silver sulphite begins to come down. The following equations show what takes place:—



The hydroxylamine which here, as always, accompanies the hyponitrite at its formation, may be represented as coming from the hyponitrite or the nitrososulphate by a process of hydrogenisation:—



The nitrososulphate which we used for our experiments was both analysed and tested qualitatively. On decomposing a quantity of it weighing 1.4222 gram by slightly acidifying its solution with hydrochloric acid, evaporating, igniting, moistening with sulphuric acid, and again igniting (in order to transform a little chloride produced during the evaporation with hydrochloric acid), a quantity of potassium sulphate was obtained corresponding with 79.27 per cent. Calculation indicates 79.82 per cent. The salt analysed was only air-

dried and was slightly damp. Some of it left in a desiccator for 16 hours lost weight and gave 79.91 per cent. sulphate; as thus prepared, although dry, it contained a little sulphate, which it did not when only air-dried. Further exposure of the dry salt in the desiccator caused no further loss in weight.

In connection with the decompositions of the nitrososulphates described in this paper, it is material to note some points in the properties of these salts. A solution of nitrososulphate, free from either sulphite or nitrite, does not affect an acidified solution of permanganate. Our preparation was certainly free from both these salts when used. When heated moist, nitrososulphate gives off nitrous oxide, as Davy observed, and becomes sulphate with no trace of sulphite. When heated dry, it changes to nitric oxide and sulphite again, as observed by Pelouze.

The attempts we have made to reconvert hyponitrite and sulphite to nitrososulphate by the use of iodine, in imitation of Spring's reactions, have been failures hitherto.

XXX.—*The Constitution of some Non-saturated Oxygenous Salts, and the Reaction of Phosphorus Oxychloride with Sulphites and Nitrites.*

By EDWARD DIVERS, M.D.

THE object of the present paper is to show that non-saturated oxygenous salts differ from those which are saturated, not in the manner in which they are universally represented as doing—namely, in having their chlorous elements of a lower than their maximum valency—but in being less oxylic than the saturated salts of the same element, or, in the case of metallic salts of monobasic acids, not oxylic at all.

Sulphites—no Evidence that they are Dioxylic.

Two views have been held concerning the constitution of sulphites as salts. According to the one, they are half haloid salts, half oxylic, as represented by the formula $\text{Ag} > \text{SO}_2$. This view was proposed by Odling very many years ago, but has long since been given up by him for the other.* According to this view, the constitution of

* It was also held by Strecker and others, and in England the late Henry Watts

sulphites is the same as that of sulphonates, and may therefore be for brevity called the *sulphonic* constitution.

On the other view, sulphites are dioxylic, as represented by the formula $(\text{AgO})_2\text{SO}$. This view is now generally accepted, in spite of several well-known reactions not in harmony with it.

The reasons for this acceptance seem to be mainly two—one that the sulphites are so much less stable than the sulphonates; the other, the conviction that all oxygen salts are oxylic salts, including sulphites, considered to have been proved such by experiments with phosphorus pentachloride and oxychloride.* Of these reasons, I shall discuss the latter first, so far at least as it rests on experimental evidence in the case of the salts in question.

Action of Phosphorus Pentachloride on Sulphites.—From the time of the successful application of the chlorides of phosphorus by Gerhardt, Cahours, and others, in the investigation of the constitution of organic acids, the adaptability of these reagents for a similar purpose in inorganic chemistry has been assumed, but has been only very imperfectly established by experiment. However, among the salts examined are the sulphites, and these we learn have yielded results with both the pentachloride and the oxychloride of phosphorus, leading to the conclusion that sulphites are dioxylic compounds of the radicle thionyl, as represented by the formula for silver sulphite, $(\text{AgO})_2\text{SO}$.

On the authority of Carius,† phosphorus pentachloride heated with a sulphite yields thionyl chloride, Cl_2SO . I have not thought it necessary to verify this statement, as I see no grounds for doubting its accuracy. I have only to show that this formation of thionyl chloride has no significance whatever in determining the constitution of a sulphite. The thionyl chloride comes assuredly from a secondary reaction after the decomposition of the sulphite has been effected. To insist that it does not would require us to admit that an organic sulphonate is also a thionyl compound. For when the pentachloride is heated at 120° with sodium ethanesulphonate, thionyl chloride is the sulphur-product. But, as Carius, who observed this, has shown that ethanesulphonic chloride is normally formed at first—

in his last edition of *Fownes' Organic Chemistry*, adopted it, suggesting, however, the existence of sulphites of both one and the other constitution. Michaelis and Landmann also give the sulphonic constitution to metallic sulphites, while leaving to selenites the dioxylic one. So also, in one place, Takamatsu and Smith use the sulphonic formula in their paper on pentathionic acid.

* Another reason is probably to be found in the old-established notion that oxygen salts are always built up of an oxidised basylous and an oxidised chlorous radicle.

† Roscoe and Schorlemmer's *Treatise*. The correctness of this reference to Carius is doubtful. See next note.



and then spontaneously decomposes—slowly in the cold, more rapidly when heated—into sulphur dioxide and chlorethane, and has further shown that phosphorus pentachloride readily converts sulphur dioxide into thionyl chloride, the question of the sulphonic constitution is not touched by this derivation of thionyl chloride from a sulphonate. The corresponding production of thionyl chloride, observed by Barbaglia and Kekulé, on heating benzenesulphonic chloride with phosphorus pentachloride at 200° , should receive a similar explanation rather than the one proposed by Michaelis, in which sulphuryl chloride appears as a transition-body.

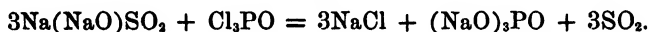
If we now conceive a sulphite as having the constitution, not of a dioxylic salt, but of a sulphonate, its reaction with phosphorus pentachloride will give as a transition-product a metallic chlorosulphonate, say ClNaSO_2 , and this will certainly at once be decomposed into metallic chloride and sulphur dioxide; the latter will then be acted on by more pentachloride and changed into thionyl chloride.

Action of Phosphorus Oxychloride on Sulphites.—A statement occurs in *Odling's Manual of Chemistry* that thionyl chloride is produced by the action of oxychloride of phosphorus on metallic sulphites, and in *Watts's Dictionary* Carius is given as the authority for this statement.* The objection to the use of phosphorus pentachloride as a test of the constitution of an acid is that its action may extend not merely to the oxylic oxygen but also to the oxygen of the radicle, or that which is non-oxylic. This objection cannot be made against phosphorus oxychloride, which apparently can be charged by no possibility with confounding the two kinds of combined oxygen, except in the very rare case, as with boron oxide at high temperatures, of its reversion to the pentoxide and pentachloride from which it has, or may have, been formed. It cannot be denied, therefore, that the production of thionyl chloride from a sulphite by the action of phosphorus oxychloride would prove the constitution of a sulphite to be that of a thionyl compound. Recognising this, and at the same time seeing the weight of evidence there is that sulphites

* *Annalen*, 70, 297. Here, in Japan, I cannot refer to the *Annalen* to verify this statement. But although the first volume of Liebig and Kopp's *Jahresbericht* gives statements from the earliest pages of vol. 70 of the *Annalen*, it contains no mention of Carius, whose name does not appear in the *Jahresbericht* until some years later. In the *Annalen*, 106, 307, he gives the action of phosphorus pentachloride, not of oxychloride, on a *sulphate*. Possibly, therefore, Carius is credited with this statement by mistake. [A mistake has been made. The paper referred to is entitled: "Ueber Schwefligsaures Phosphorchlorid; von P. Kremers," and describes the action of PCl_5 on SO_2 , the product examined being it is now obvious a mixture of SOCl_2 and POCl_3 .—H. E. A.]

have not this constitution, I had some experiments made by Mr. Tetsukichi Shimidzu, M.E., who has kindly given every care to the matter, including that of preparing the oxychloride and the sulphites.

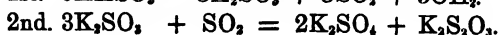
The sulphites selected were those of lead, calcium, and sodium. Trials were repeatedly made with each of these sulphites and the oxychloride, but in no instance could any thionyl chloride or other oxychloride of sulphur be obtained. The sulphite remained for the most part unchanged, but was partly converted into sulphur dioxide, together with chloride and phosphate of the metal. Most of the unaltered phosphorus oxychloride which distilled over condensed in the well-cooled receiver, but a little of it escaped as vapour along with the sulphur dioxide. When treated with water, this gas gave, therefore, a chlorine reaction, but it also gave a phosphoric acid reaction. The condensed phosphorus oxychloride appeared to be pure, and gave neither sulphur dioxide nor sulphuric acid with water. As thionyl chloride boils to 82° , it would, if formed, have been present in this liquid. The reaction which takes place is no doubt as follows:—



So far, then, from proving the dioxylic structure of sulphites, the action of oxychloride of phosphorus furnishes, perhaps, direct evidences of their sulphonic character. It is probable, however, that thoroughly dry and pure sulphites are not acted on at all by pure phosphorus oxychloride.

Sulphites—Evidence that they are not Dioxylic.

Action of Heat on Sulphites.—It has been known for a very long time that sulphites yield sulphides and sulphates when heated. Quite recently, Geuther has materially added to our knowledge of the change which then takes place, by examining the effect of heat on potassium hydrogen sulphite.* He finds that at 190° this salt gives off water and sulphur dioxide, and leaves a mixture of two molecular proportions of sulphate to one of thiosulphate. The explanation of this appearance of thiosulphate is clearly that the acid sulphite becomes normal sulphite, sulphur dioxide, and water, in the first place, and that then one molecule of sulphur dioxide reacts with three molecules of normal sulphite to form two molecules of sulphite and one of thiosulphate, thus:—



As Geuther points out, the thiosulphate when strongly heated yields

* Pyrosulphite with water of crystallisation (Berthelot).

sulphate and the sulphide hitherto recognised as a product of the operation.

Taking into consideration the conclusive evidence there is of thio-sulphate having half its sulphur in place of half the oxylic oxygen of a sulphate, the formation of either thiosulphate or sulphide from a sulphite by heat points unmistakably to a constitution for sulphites in which the metallic radicle is partly in direct union with the sulphur, since with a dioxylic structure—that is, with both metal and sulphur oxidised—no mode of reaction is open by which a sulphide could be formed.*

Experiments on the Decomposition of Sulphur Dioxide by Alkali Sulphites.—Wishing to test the accuracy of the assumption I have made in the preceding paragraph and the foot-note to it, that sulphur dioxide is resolved into its elements by hot sulphites, I have got Mr. Shimidzu to heat dry sodium sulphite in dry sulphur dioxide. His results are interesting and entirely confirmatory of my assumption.

The sulphite used, after being dried in the air at about 90°, was found to contain a little sulphate, and to dissolve in water to a clear solution, remaining so after acidification. Some of this salt was kept for half an hour at a temperature of 190°, and again tested. It was unchanged. Other portions were then heated in sulphur dioxide for ten minutes at 190°, air being excluded and the sulphur dioxide dry. Temperatures near 190° were employed, because at this temperature Geuther obtained the sulphate and thiosulphate.

A small sublimate of sulphur was thus obtained, and besides, sufficient sulphur remained intermixed with the sulphite to render its solution milky. A little thiosulphate was also formed, and very distinctly more sulphate than the small quantity present before the experiment.

From this it is clear, first, that alkali sulphite moderately heated decomposes sulphur dioxide, taking its oxygen to form sulphate, and

* Geuther states that the pyrosulphite ($K_2S_2O_6$) also yields thiosulphate. But this is opposed to Berthelot's precise statement that the pyrosulphite yields only sulphate, sulphur dioxide, and sulphur, since if thiosulphate were formed, it would leave sulphide. Berthelot's finding seems the more probable:—



one molecule of the sulphur dioxide yielding free sulphur, and giving up its two atoms of oxygen to two molecules of normal potassium sulphite. The normal sulphite if heated strongly also yields sulphate and polysulphide, a fact recently confirmed by Geuther. Here, of necessity, alkali oxide must be formed, although not mentioned, probably combined with the material of the crucible. In this case too, therefore, we have sulphur dioxide at our disposal to account for the change by its reaction with undecomposed sulphite.

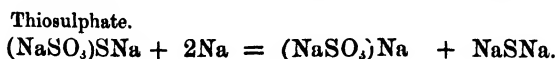
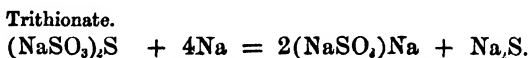
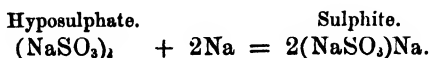
rejecting the sulphur,* when the dioxide is in large excess; and secondly, that it also takes the sulphur to form thiosulphate when the sulphur dioxide is present only in limited quantity.

The experiments, which were several times repeated, were not of long duration, as in that case errors might have arisen through some action of entering air, or some very slow dissociation of the sulphite, and thus the value of the results would have been lessened. We relied on the characteristic silver test in proving the presence of thiosulphate.

The Quinine Test for Non-oxylic Salts.—Stokes (this Journal, **22**, 174) has pointed out that a haloid or non-oxylic salt not only does not form a strongly fluorescing salt with quinine, but even quenches the fluorescence of an oxylic salt of that base. He did not examine sulphites, but Mr. Shimidzu and I find that a solution either of a sulphite or of sulphur dioxide, added to a sulphuric acid solution of quinine, at once destroys the fluorescence, and therefore, to the extent to which this test is trustworthy, proves that it contains a (partly) non-oxylic acid.

Double Sulphites of Silver.—Silver sulphite dissolves in alkali sulphites to form double sulphites. Alkali sulphites freely dissolve even silver chloride. Now, since silver does not form double salts of acids which are exclusively oxylic,† and very readily forms double salts of haloid acids, this property of silver sulphite is evidence of its being (partly) non-oxylic.

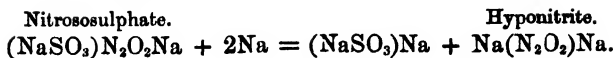
Conversion of certain other Salts to Sulphites by Sodium, and of Sulphites to other Salts by Chlorine or Iodine.—The now well-known results obtained by Otto, Spring, and others, by the action of sodium-amalgam on alkali hyposulphates, trithionates, and thiosulphates, only require to be formulated in order to show undeniably that sulphites are not dioxylic:—



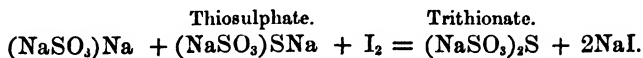
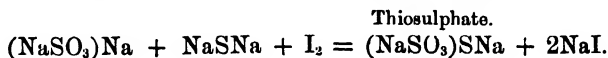
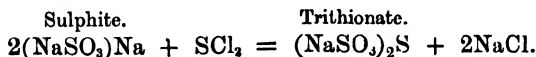
To these I may add the reaction observed by Mr. Haga and myself (p. 203):—

* Sulphur dioxide, in like manner, is deoxidised by hypophosphorous and phosphorous acids (Ponndorf), and by phosphenylic acid (Michaelis and Ananoff).

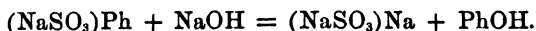
† [See, however, Russell and Maskelyne, *Proc. Roy. Soc.* (1877), **26**, 357.—H. K. A.]



Spring's observations on the effects of sulphur chloride and of iodine on sulphites alone, and these salts in admixture with sulphides and with thiosulphates, are equally conclusive:—



The Interrelations of Sulphites with Sulphonates and Sulphinates.—There are no facts more decisive as to the non-dioxylic structure of sulphites than those I have now to adduce, so familiar to chemists. The conversion of an organic sulphonate into a metallic sulphite, by fusing it with alkali hydroxide, is one of its earliest known reactions:—



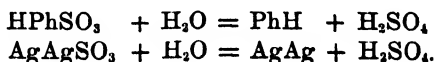
In order to avoid the use of this direct expression of the change, and to write a sulphite as a thionyl compound, we must leave facts for fancy, and regard alkali hydroxide as *deoxidising* an acid radicle, that is, sulphuryl to thionyl.

As the complement of this reaction of a sulphonate, there is Strecker's reaction of a sulphite, as modified by Hemilian, in which in aqueous solution the sulphite becomes sulphonate:—



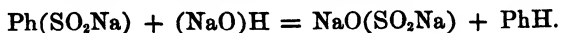
Either this equation represents the change, or the remarkable assumption must be made that phenyl chloride can bring about the oxidation of thionyl to sulphuryl.

While sulphonates can be hydrolysed to sulphuric acid (Armstrong and Miller), one sulphite at least can be similarly hydrolysed, the metal of which is more stable when free than are its oxygenous compounds. Compare silver sulphite with benzenesulphonic acid:—



Yet again does the conviction force itself upon one that sulphites, sulphonates, and sulphates have all one radicle, sulphuryl. For just as a sulphonate is related to a sulphate in Armstrong and Miller's

reaction, so is a sulphinate related to a sulphite in the reaction observed by Otto and Ostrop to take place at 250—300° between sodium benzenesulphinate and sodium hydroxide:—

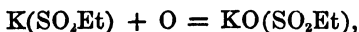


It may be added that as in the group $\text{—SO}_2\text{Na}$ the sodium is replaceable by chlorine, its constitution cannot be —(SO)ONa ; so that the above reaction shows the constitution of a sulphite to be $\text{NaO}(\text{SO}_2)\text{Na}$ no less clearly than does the reciprocal convertibility of sulphites and sulphonates.

Sulphites—their Relative Instability to be Accounted for by the Presence of their Unoxidised Metallic Radicle.

As I stated at the beginning of this paper, one of the reasons which have prevented the adoption of the same constitution for sulphites as for sulphates, is the instability and oxidisability of the former, as compared with the stability and non-oxidisability of the sulphonates. Recent experiments by Prinz extend this difference; for he has found that a sulphonate, unlike a sulphite, does not combine with sulphur.

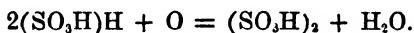
The different behaviour of sulphites and sulphonates is, however, much more probably due to difference in composition than to difference in constitution. Sulphites have half their metal united directly to the sulphur of sulphuryl, and this part of the metallic radicle it is which readily combines with unoxidised sulphur, with oxygen, or with nitric oxide. Sulphonates, on the other hand, are not oxidisable because they have hydrocarbon in place of the unoxidised part of the metal of sulphites, and this hydrocarbon does not reject direct union with sulphuryl for that with oxygen or sulphur. Again, potassium ethanesulphinate is oxidisable to sulphonate, without—and this is admitted, be it remembered—change of the sulphuryl, but by the interposition of oxygen between the metal and the sulphur, as thus represented:—



whilst sulphones, which have the same constitution as sulphonates, are not thus oxidisable, because instead of a metallic radicle they have a second hydrocarbon radicle. Ethyl sulphides do not, like alkali sulphides, oxidise in the air. It is just their sulphonic constitution, then, which makes sulphites, like soluble sulphides,* oxidisable and unstable.

* In a recent communication to the Society on the origin of thiosulphates, I have given experimental evidence that in the atmospheric oxidation of soluble sulphides it is the hydrogen or basylous radicle which oxidises, not the sulphur.

Thus interpreting the significance of the oxidisability of sulphites, we find evidence of the existence of free sulphurous acid (hydrogen sulphite) in moist or dissolved sulphur dioxide, because this is readily oxidisable whilst dry sulphur dioxide is not, except by active oxygen. When moist it has become partly changed into sulphurous acid of the formula $\begin{smallmatrix} \text{HO} \\ \text{H} \end{smallmatrix} > \text{SO}_2$, and contains, therefore, unoxidised hydrogen. Its slow oxidation to hyposulphuric acid (Jacquelain) is still more conclusive:—



Where the metallic radicle, as in the case of silver sulphite, is not an oxidisable one, the instability of the sulphite is of another order, one that has been explained on a previous page.

Sulphites not being Dioxylic, there is no Evidence that Sulphur is Sexvalent towards Oxygen.

That sulphur is bivalent when not directly combined with a more chlorous element, such as oxygen or chlorine, is universally admitted. That it is quadrivalent in some, if not all of its compounds, when it is so combined, is shown by the existence of the sulphines, and by the evidence of the existence of sulphur tetrachloride at low temperatures. Pointing quite as clearly to the same conclusion is the fact of the formation of thionyl chloride, effected by Michaelis and Schifferdecker, by the action of sulphur trioxide on sulphur tetrachloride (sulphur chloride and chlorine in a freezing mixture).

But the removal, here attempted to be made, of the distinction hitherto conceived to exist between the constitution of sulphites and sulphonates, taken in connection with the fact of the intimate relations of sulphates to sulphonates, raises the question whether sulphur is ever sexvalent towards oxygen,* as commonly supposed, and not always quadrivalent.

It is certainly a fact significant of the weakness of the case for sulphur being ever sexvalent, that for so many years Pelouze's nitrosulphate, a body of undetermined and apparently unique constitution, should have done duty as the stock illustration of this relation of sulphur. It has done so, of course, only for the want of a better.

Berthelot finds the peroxide of sulphur discovered by him to have the formula S_2O_7 . The existence of such a compound, although not

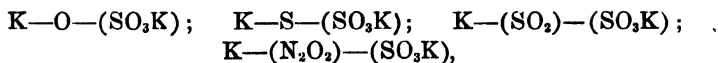
* Dehu's compounds of ethylene bromide with the sulphides of ethylene and of ethyl, and Dobbin and Masson's recently described halogen compounds of trimethylsulphine seem to show that sulphur can be sexvalent in presence of hydrocarbon radicles.

necessarily inconsistent with the quadrivalency of sulphur, must nevertheless give a certain degree of improbability to it. But then there is the strongest reason furnished, both by analogy and by the general character of sulphur compounds, to receive with doubt any evidence of the existence of a peroxide of sulphur having an odd number of oxygen-atoms along with a symmetrical constitution. An oxide with the formula S_2O_3 , probably S_4O_6 , is indeed known, but it is certainly not a symmetrical oxide, or compound of equally oxidised sulphur-atoms. Berthelot gives S_2O_3 in his list of formulated oxides, but this only represents the group seen in the formulæ of hyposulphates and pyrosulphites when written K_2O, S_4O_6 and K_2, S_2O_6 , respectively. On the other hand, evidence of the existence of a peroxide, SO_4 , having 4 atoms of oxygen to the atom of sulphur, would be welcome as matching the sulphur, selenium, and tellurium compounds with sulphur trioxide. Moved by these reasons, then, we might fairly be led to entertain doubts as to the trustworthiness of the analytical results obtained by Berthelot, did he not express confidence in their accuracy, especially if we consider the difficulty of bringing such a substance in contact with reducing agents without thereby causing oxygen to be set free. It does not, however, seem too much to assume that, since the peroxide is constantly losing oxygen when prepared, and is being decomposed during its preparation by the very means employed to make it, as in the case of ozone, it will, if only S_2O_7 , when single and perfect, scarcely yield the full 7 atoms of oxygen as the samples of it analysed were found to do. I may therefore be allowed to suggest that, in spite of all his skill, even such a veteran chemist as Berthelot may have only succeeded in preparing and analysing the peroxide when mixed with nearly half its weight of trioxide, and thus have found only 7 atoms instead of 8 of oxygen to every 2 atoms of sulphur.

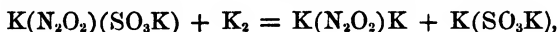
The octosulphates and lesser polysulphates quite recently described by R. Weber belong apparently, as chemical compounds, to the same category as hydrates, and do not, therefore, concern my present thesis.

Returning now to a consideration of the nitrosulphates as examples of compounds of sexvalent sulphur. To make them serve as such, they are written $S^{VI}O(OK)_2(NO)_2$. But as they are formed from sulphites by adding nitric oxide, just as sulphates are formed by adding oxygen to sulphites, thiosulphates by adding sulphur, and pyrosulphites by adding sulphur dioxide* (even in presence of water), the four salts may be written uniformly, thus:—

* The radicle SO_2 can enter here between the metal and the (SO_3K) , it may be concluded, because SO_2 in combination with (SO_3K) must be more chlorous than SO_2 in combination with (OK) .



and since the nitrosulphates can be thus written, they have no superior value to sulphates or thiosulphates in establishing that sulphur is sometimes sexvalent. The reaction between these salts and the alkali metals, observed by Mr. Haga and myself,

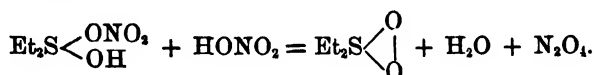


shows that this view of their constitution is the proper one to take.

The Double Atom of Oxygen as a Radicle.—Nitrosulphates being no longer of value in determining the valency of sulphur, it becomes of greater interest than before to consider whether sexvalency or quadrivalency is shown by sulphur in sulphates. This point may be discussed in a very few words. If it is to be treated as anything more than a question of graphic representation, there cannot be much difficulty in deciding that sulphur behaves as a quadrivalent element in sulphates and all other sulphuryl compounds. For the same reasons which have led to the adoption of the view that sixteen, and not eight parts, by weight, of oxygen form in chemical change an indivisible part of a molecule of water or of a molecule of alcohol, must lead, if consistency is to be preserved, to the conclusion that the two atoms of oxygen in sulphuryl form a double atom, or single bivalent quantity, in the constitution of this and of some other chlorous radicles. Thus, there are no stages or breaks in the formation of compounds of sulphuryl as regards this radicle itself, and none in their decomposition, the sulphur taking up or losing its own weight of oxygen in one operation. In other words, sulphuryl compounds are not reducible to thionyl compounds, and thionyl compounds are not directly oxidisable to sulphuryl compounds, the special case of the conversion of the free oxides into each other being excepted. Thus, in ethanesulphonic chloride, or in a sulphone, reduced by a hydrogen mixture, the sulphuryl loses all its oxygen at once. Again, the radicle of sulphuryl hydroxychloride is either wholly removed, or not touched at all by hydrogen sulphide, $8\text{SO}_2(\text{OH})\text{Cl} + 5\text{SH}_2 = 6\text{SO}_2(\text{OH})_2 + 6\text{HCl} + \text{S}_2\text{Cl}_2 + 5\text{S}$ (H. Prinz). The production of thionyl chloride from ethanesulphonic chloride and from benzenesulphonic chloride by phosphorus pentachloride has already been mentioned as being really a reaction between free sulphur dioxide and the pentachloride. But it is also stated in some books that Michaelis has found sulphuryl chloride to be slowly converted to thionyl chloride by phosphorus pentachloride. It must, however, be taken into consideration that this chemist has shown that phosphorus pentachloride decomposes sulphuryl oxychloride, $\text{S}_2\text{O}_2\text{Cl}_2$, into sulphur dioxide and chlorine; and

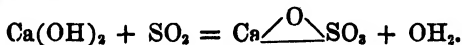
that sulphuryl chloride cannot be formed by means of phosphorus pentachloride, chlorine and sulphur dioxide (and not thionyl chloride) being produced instead. Any slow formation of thionyl chloride from sulphuryl chloride may, therefore, be attributed to a dissociation of the sulphuryl chloride into sulphur dioxide and chlorine in the first place, and then to the conversion of the dioxide into thionyl chloride by Schiff's well-established reaction.

An apparent exception to this statement of the non-oxidisability of thionyl to sulphuryl may occur to some in the case of ethylsulphine oxide, a thionyl compound capable of being oxidised to ethyl sulphone, a sulphuryl compound. As a fact, this oxide forms a well-defined nitrate, and this nitrate it is which, heated with nitric acid, yields the sulphone, thus:—



Another apparent exception will be the conversion of sulphuric acid to sulphur dioxide by hot reducing agents. But here the sulphuric acid may be confidently assumed to first undergo dissociation into sulphur trioxide and water.

The Constitution of Sulphur Dioxide.—With regard to the conversion of sulphur dioxide to sulphur trioxide, I need merely point out that this occurs only under circumstances which serve as conditions for the development of active oxygen, and just those, therefore, which give us the double atom of oxygen, to be found in ozone, $\text{O} \begin{array}{c} \diagup \quad \diagdown \\ \text{O}_2 \end{array}$,* and hydrogen dioxide, $\text{H}_2 \begin{array}{c} \diagup \quad \diagdown \\ \text{O}_2 \end{array}$, substances produced also in such circumstances. It is to be noted of sulphur dioxide that it is in fact a body intermediate between sulphuryl and thionyl compounds, and may be considered either as $\text{S} \begin{array}{c} \diagup \quad \diagdown \\ \text{O}_2 \end{array}$ or $\text{O}:\text{S}:\text{O}$ as commonly treated. There is much to favour the view contained in the first of these formulæ. Thus, this being accepted, the union of sulphur dioxide with a base becomes similar to that of chlorine:—



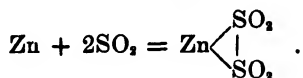
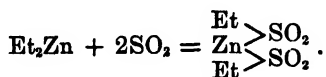
Again, zinc ethide unites directly with sulphur dioxide to form

* As a means of simplifying the writing of many formulæ, I think the symbol $\begin{array}{c} \diagup \quad \diagdown \end{array}$ very convenient, and would therefore recommend its use. Thus, we may write

$\text{O}(\text{NO})_2$, but $\text{O} \begin{array}{c} \diagup \quad \diagdown \\ (\text{FeO})_2 \end{array}$, instead of $\text{O} \begin{array}{c} \text{FeO} \\ | \\ \text{FeO} \end{array}$; and $\text{O}(\text{CH}_3)_2$, but $\text{O} \begin{array}{c} \diagup \quad \diagdown \\ (\text{CH}_3)_2 \end{array}$ instead

of $\text{O} \begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$.

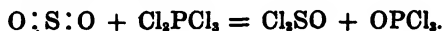
ethane-sulphinate, and so, apparently, does zinc itself to form hyposulphite (Bernthsen), although in this case in the presence of water:—



Sulphur dioxide is reducible by zinc and acid to the simple hydride, —S◀ to S : H,—whilst the double atom of oxygen in sulphuryl compounds is not thus replaceable by hydrogen as it is in nitroxyl compounds, just for the reason that the atom of sulphur becomes fully saturated by two atoms of hydrogen, and cannot therefore take these when it is already in combination with other radicles. Where the attempt to force it to do so gives a result, as is usually the case,—for example, when ethanesulphonic chloride is treated with a hydrogen mixture,—the two atoms of oxygen are removed without being displaced by hydrogen, this element merely taking the place of the chlorine removed at the same time:—



The reaction, however, which, for the present at least, must be regarded as establishing the formula O : S : O, is that of phosphorus pentachloride on sulphur dioxide—



but it stands alone.

Sulphites—their Place in a Series of Sulphuryl Compounds.

A brief review of sulfoxy-compounds considered as combinations of the radicles sulphuryl and thionyl may serve to strengthen the view that sulphites are not dioxylic. The conception of a compound radicle as a something in the composition of a molecule which is as much indivisible in many of the relations of the molecule as an atom, has apparently been much weakened by the doctrine of valency. Yet there is no sufficient reason for this. To see but little else in the property of phosphorus trichloride of combining with either two univalent chloride-atoms or one bivalent oxygen-atom than that phosphorus is quinquivalent, is to ignore the almost entire want of connection in properties between the pentachloride and oxychloride, and the fact that the latter is one of a series of compounds of a tri-

valent radicle phosphoryl as well defined as that of the compounds of a simple radicle. It would, indeed, be easy to show that it has been the failure to appreciate the connections of facts expressed by the theory of compound radicles which has done most to bring the theory of valency into disrepute.

Compounds of Sulphuryl, =S<O_2 .

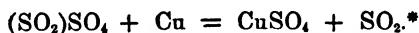
Sulphuric oxide, gaseous ..	O : SO_2 .
Sulphuric oxide, condensed.	$\text{O}_2\text{S : O}_2\text{ : SO}_2$.
Thiosulphuric peroxide....	$\text{O}_2\text{S<}\overset{\text{O}}{\underset{\text{S}}{\text{=}}}\overset{\text{O}}{\text{S}}\text{>SO}_2$.
Sulphuric peroxide, if SO_4 .	$\text{O}_2\text{▷SO}_2$.
[Sulphuric peroxide, if S_2O_7 (?)	$\text{O}_2\text{S<}\overset{\text{O}}{\underset{\text{O}}{\text{>}}}\text{SO}_2$ or $\text{O}_2\text{S<}\overset{\text{O}-\text{O}}{\text{>}}\text{SO}_2$].
Sulphates	$(\text{KO})_2\text{SO}_2$; $\overset{\text{EtO}}{\text{KO}}\text{>SO}_2$; $(\text{EtO})_2\text{SO}_2$.
Thiosulphates.....	$\overset{\text{KO}}{\text{KS}}\text{>SO}_2$; $\overset{\text{KO}}{\text{EtS}}\text{>SO}_2$.
Nitrososulphates	$\overset{\text{KO}}{\text{K(N}_2\text{O}_2)}\text{>SO}_2$.
Pyrosulphites	$\overset{\text{KO}}{\text{K(SO}_2)}\text{>SO}_2$.
Pyrosulphates	$\overset{\text{KO}}{\text{O}}\text{>SO}_2$; $\text{KO}>\text{SO}_2$.
Monothiopyrosulphates (tri- thionates), and	$\overset{\text{KO}}{\text{S}}\text{>SO}_2$; $\overset{\text{KO}}{\text{S}_2}\text{>SO}_2$.
Dithiopyrosulphates (tetra- thionates)	$\overset{\text{KO}}{\text{S}_2}\text{>SO}_2$.
Hyposulphates	KOSO_2 KOSO_2
Sulphites and sulphonates.	$\overset{\text{KO}}{\text{K}}\text{>SO}_2$; $\overset{\text{KO}}{\text{Et}}\text{>SO}_2$; $\overset{\text{EtO}}{\text{Et}}\text{>SO}_2$.
Thiosulphites or thiosul- phonates	$\overset{\text{EtS}}{\text{Et}}\text{>SO}_2$.
Hyposulphites	KSO_2 ; KSO_2 ; (?) $\overset{\text{EtSO}_2}{\text{EtSO}_2}$.
Sulphinates and sulphones.	$\overset{\text{Et}}{\text{K}}\text{>SO}_2$; Et_2SO_2 .

Sulphuric Oxide Condensed.—The formula S_2O_6 , adopted for this body by Michaelis, brings it into relation with the pentoxides of

nitrogen and phosphorus as bodies of the same type as their own salts:—

Nitroxyl nitrate	$(O_2N).O.NO_2$	like $KONO_2$
Sulphuryl sulphate	$(O_2S):O_2:SO_2$	„ BaO_2SO_2
Phosphoryl phosphate	$(OP):O_3:PO$	„ AlO_3PO

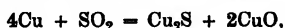
The reaction of sulphuric acid with mercury, copper, or silver, in which all the hydrogen of the acid is left as water, is to be treated as one occurring between the metal and sulphuryl sulphate, S_2O_6 , into which and water sulphuric acid so readily dissociates, and is expressed by the equation—



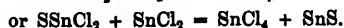
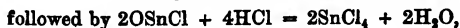
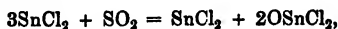
Action of Sulphur Dioxide on Sulphites (this vol., p. 209).—To represent the reaction as occurring, in the first place, directly between the sulphuric acid and the metal, and then between *nascent* hydrogen and more of the acid, is a proceeding which will not bear criticism. It is opposed to the fact that metals of this class never do liberate hydrogen, and to the consideration that were hydrogen thus liberated it must, in order to be active, be assumed to have greater chemical power than the agent which set it free, and that, too, in order to enable it to recombine with oxygen immediately after having been separated from this very element.

Thiosulphuric Peroxide.—If the two common oxides of sulphur have

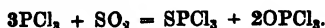
* At a sufficiently low temperature, as shown by the thorough examination made by Pickering into the behaviour of copper with sulphuric acid, copper sulphide is formed. This formation I attribute to the decomposition of sulphur dioxide into oxygen and sulphur, which each combine with copper, thus:—



the CuO then becoming sulphate. At higher temperatures, the sulphide is also decomposed by the sulphuric acid. In support of this view, I may refer to the action of sulphur dioxide on stannous chloride or on phosphorous chloride, in both of which actions the dioxide is similarly decomposed, and its elements distributed among three molecules, thus:—



In the case of phosphorous chloride:—



This reaction, however, occurs only at a red heat, but then that with thionyl chloride takes place at lower temperatures (Michaelis):—



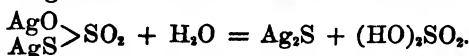
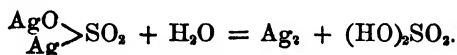
See also a former paragraph.

the constitution represented by the formulæ $O : S : O$ and $O_2 \triangleright S : O$, a peroxide may be looked for as able to exist, having the constitution $O_2 \triangleright S \triangleright O_2$. Unless Berthelot's peroxide contains this body, it is not yet known, but the compounds of sulphuric oxide with sulphur, selenium, and tellurium, examined by R. Weber, and by Shimose and myself, appear to answer both in composition and properties to this peroxide with one atom of oxygen displaced by quadrivalent sulphur, selenium, or tellurium, and will, therefore, form a double molecule of the oxide, as shown by the formula in the table (see also *Trans.*, 1884, 195).

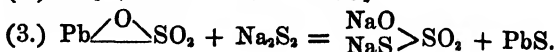
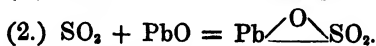
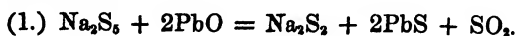
Sulphuric Peroxide.—The formulæ I have suggested in the table for Berthelot's peroxide, if S_2O_7 , are fanciful, but the only ones consistent with the view that sulphur is not more than quadrivalent. These formulæ are calculated to confirm the doubts which must be entertained of the existence of an oxide with such a composition. The formula for the peroxide as SO_4 has been noticed in the previous paragraph, and leaves the sulphur quadrivalent.

Thiosulphates.—It is impossible to represent in a simple manner the formation of thiosulphates from sulphites, unless the latter salts are formulated as monoxylie.

The analogy of the decompositions of silver sulphite and silver thiosulphate by water, is worthy of notice here, as illustrating the uniform valency of sulphur in these salts and in sulphates:—



Böttger, like Berthelot, has found that other metallic oxides besides that of copper produce thiosulphates from alkali polysulphides. These reactions are all essentially forms, I consider, of that which takes place between sulphur and lime when heated with water, and which, in a recent paper, I have interpreted as being—(1) the formation of sulphur dioxide (sulphuryl) along with sulphide of the metal, (2) the union of the dioxide with base, and (3) the conversion of sulphite to thiosulphate. Thus, taking the case observed by Böttger, that of lead oxide (hydroxide) and sodium pentasulphide, I would express it somewhat like this:—



Böttger sees in the effect of lead oxide on alkali tetra- and penta-

sulphides proof that these bodies are not the sulphur analogues of sulphites and sulphates. This effect, however, goes no farther than to show how much more readily reducible the polysulphides are than the sulphites and sulphates.

Nitrososulphates.—The constitution of these salts as sulphur compounds has already been noticed. As nitrogen compounds, their constitution will be further considered under nitrites.

Pyrosulphites or Sulphurylsulphates.—From Berthelot's experiments it seems very doubtful whether any true acid sulphites exist, that is, which are other than the pyrosulphites with water of crystallisation.

To represent pyrosulphites, as is done in the table, as having the group SO_2 between half the metal and the sulphuryl, is in accordance with accepted views about anhydro-salts. Since sulphur dioxide in entering into combination behaves in all other cases as sulphuryl, it probably does so here, and therefore stands in the pyrosulphites with its sulphur joined to metal, thus:— $\text{K}-\overset{\text{O}_2}{\text{S}}-(\text{SO}_3\text{K})$, making these salts to be intermediate between hyposulphates and hyposulphites:—



Accordingly, just as disulphuryl, S_2O_4 , unites with a metal peroxide to form the first, and with a metal to form the last, so it unites with a metal monoxide to form a pyrosulphite (even in presence of water). Pyrosulphites may however be thionylsulphates:— $\text{KO}-\text{S}-(\text{SO}_3\text{K})$, although most probably they are not.

The reality of this intermediate position is further shown by the facts that a pyrosulphite can be reduced by zinc or sodium to hyposulphite, and can be oxidised by lead dioxide, or by chloral, and other chloromethylic compounds to hyposulphate (Rathke).

Dithiopyrosulphates.—The double atom of sulphur in these salts, although hardly of noticeable occurrence in inorganic chemistry, is a well-marked and stable radicle in the organic bisulphides.

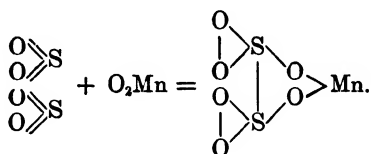
Hyposulphates.—Some chemists* adopt for these salts a formula different from that here given to them, in which they appear as thionyl compounds, thus:— $(\text{KO}.\text{SO})_2 \triangleleft \text{O}_2$. But surely there is incongruity in the notion of peroxidised thionyl compounds, whilst there are no facts in the history of these salts which suggest such a view of their constitution.

Hyposulphates are also called dithionates, but this name, in so far as it indicates relationship to the other polythionic salts, is unsatis-

* Roscoe and Schorlemmer, *Treatise on Chemistry*.

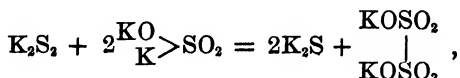
factory, whereas the older name of hyposulphates is perfectly appropriate in the set of names—sulphate and hyposulphate, sulphite and hyposulphite, as is shown by the formulæ for these salts given in the table. The other polythionic salts may be defined as those in which unoxidised sulphur unites two sulphuryl radicles, whilst hyposulphates are salts which contain no sulphur but that of sulphuryl. Hyposulphates oxidise directly to sulphates, in presence of acid, and reduce directly to sulphites in presence of base, and are strictly intermediate between these two classes of salts.

The formation of a hyposulphate by manganese dioxide is at once intelligible from the following equation:—

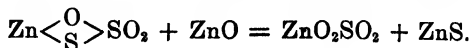


So is also its decomposition by sodium amalgam, when we use the monoxyclic formula for a sulphite, as already shown on a previous page.

Berthelot finds that both copper oxide and zinc oxide convert alkali polysulphides not only into thiosulphate, but into hyposulphate and sulphate. The formation of the hyposulphate may probably be explained as due to the action of the sulphur of the polysulphide on alkali sulphite (which substance, according to what I have argued in a previous paper to the Society, is a transition-body in the formation of thiosulphate). This sulphur partly converts the sulphite into thiosulphate, but partly also into hyposulphate, thus:—



in accordance with Spring's reactions with iodine and with sulphur chloride, already noticed in this paper. The sulphate comes probably from the decomposition of zinc thiosulphate by zinc oxide, in accordance with the behaviour which some metallic thiosulphates show:—

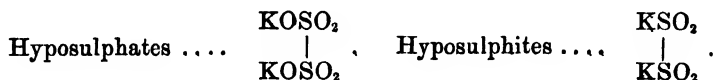


For the passage of thiosulphate to hyposulphate observed by Ramsay, see below under "*Hyposulphites*."

Sulphites and Sulphonates.—A sulphonate should be defined as an organic sulphite. The sulphurous ethers at present called sulphites should cease to receive this designation, and might be called *thionites*.

Thiosulphites or Thiosulphonates.—Pauly and Otto have so clearly established the constitution of these bodies that the provisional term, *disulphodioxides*, might well disappear from text-books.

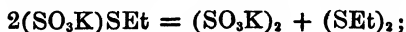
Hyposulphites.—Schützenberger makes his *hydrosulphites* to be salts of an acid H_2SO_3 . His results have been called in question by Bernthsen, but even should they prove to be correct, the salts would still be sulphuryl compounds, corresponding with the sulphinates. Bernthsen, however, has adduced evidence which seems sufficient to justify chemists in accepting the formula $\text{H}_2\text{S}_2\text{O}_4$ given by him to hyposulphurous acid, in place of H_2SO_3 . I have written the hypsulphites in the table with a formula relating them to hyposulphates in the way of haloid salts to oxylic salts, and placing them between sulphites and sulphinates just as the hyposulphates stand between sulphates and sulphites:—



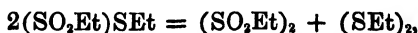
Such a constitution is a highly probable one; but without a fuller knowledge of these salts than we have at present, it cannot be regarded as established. Their mode of formation is expressed by the equation

already given:— $\text{Zn} + 2\text{SO}_2 = \text{Zn} \triangle (\text{SO}_2)_2$; also $\text{Zn} + 2 \begin{array}{c} \text{KSO}_2 \\ | \\ \text{KOSO}_2 \end{array} = (\text{KSO}_2)_2 + \text{Zn}(\text{SO}_3\text{K})_2$; and the assumption that the zinc does not take oxygen is borne out by the fact that even zinc-ethyl does not do so in the act of forming its sulphinate with sulphur dioxide. Although hypsulphites might be written as compounds of oxide of metal with sesquioxide of sulphur, they have no relation in properties to the known sesquioxide, which is a peroxidised body.

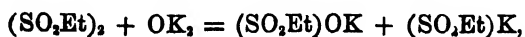
The formula for *ethyl hypsulphite*, which I have inserted in the table, is that of a body unknown in a permanent form; but that such a compound exists as a transition-body seems to follow from Pauly and Otto's researches. According to Ramsay, an ethylic thiosulphate may decompose, as follows, into hypsulphate and ethyl bisulphide:—



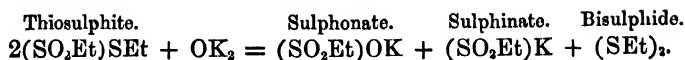
and if we assume that ethylic thiosulphite behaves in like manner, thus:—



forming hypsulphite, and that this reacts with potassium hydroxide, thus:—



we have Pauly and Otto's observed reaction :—



Sulphinates and Sulphones.—The sulphinates are less stable than sulphones, because they are compounds of unoxidised metal. In their decomposition, no partial deoxidation occurs, but the separation of the sulphur and oxygen becomes complete in one molecule, these elements then converting other undecomposed molecules into thio-sulphonate and sulphonate respectively.

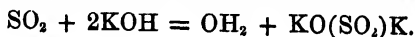
One way of forming a sulphinate is to combine sulphur dioxide with an organo-zinc compound. This fact alone goes far to prove that sulphites are monoxalic; for if zinc ethide, a powerful reducing agent, in uniting with sulphur dioxide yields a compound of sulphuryl, that is, of sulphur that cannot be further oxidised, it seems certain that an oxygenous body, such as zinc hydroxide, will, in uniting with sulphur dioxide, not yield a compound of thionyl, that is, of sulphur capable of being further oxidised.

Compounds of Thionyl, =S:O .

Thionyl oxide.....	O:SO.
Thionyl chloride.....	$\text{Cl}_2\text{SO.}$
Ethyl thionite ("sulphite")..	$(\text{EtO})_2\text{SO.}$
Ethyl potassium thionite	$\begin{matrix} \text{EtO} \\ \text{KO} \end{matrix} > \text{SO.}$
Ethyl sulphine oxide	$\text{Et}_2\text{SO.}$
(?) Thionamide	$(\text{NH}_2)_2\text{SO.}$

Thionyl oxide.—With the exception of the sulphine oxides, all thionyl compounds are readily convertible to sulphur dioxide. Thionyl chloride may be derived from sulphur tetrachloride, but it and all other thionyl compounds, except the sulphine oxides, are obtained directly or indirectly from thionyl oxide.

The formation of sulphites from sulphur dioxide, regarded as thionyl oxide, involves the occurrence of the change from that relation which exists between the sulphur and oxygen in thionyl to that which exists in sulphuryl. In whichever way sulphites are viewed, this change has to be met; but it is the practice at present to localise it, not here, but in the act of metallic sulphites passing into organic sulphites ("sulphonates"), or of these into metallic sulphites. In the conversion of thionyl oxide to a sulphite, it may be considered to be oxidised to sulphuryl by and then combined with a base, thus :—



Such an oxidation of a chlorous radicle by a base is no assumption; it is effected by potash acting on chlorine and some other simple bodies, and on benzaldehyde and other carbon compounds.

This explanation of the passage from thionyl to sulphuryl compounds is not one of the simplest, but it is much more satisfactory than any that can be devised of the interconversion of sulphites and sulphonates, on the usual supposition that the former are thionyl compounds. In the derivation of sulphites from other thionyl compounds, the intermediate production of thionyl oxide may, without doubt, be considered to take place.

Thionyl Chloride.—It seemed to me to be unnecessary to introduce the chloride and oxychlorides of sulphuryl into the list of compounds of that radicle, but thionyl chloride is of special importance amongst thionyl compounds, from its serving to fix the constitution not only of sulphur dioxide, but of the sulphurous ethers or "thionities." As is well known, these ethers can also be formed from sulphur thiochloride or thio-thionyl chloride. Prinz has recently published his conclusion that this body, S_2Cl_2 , has not the constitution of thionyl chloride, but I am unable to follow his argument. He has shown that Carius's reaction between phosphorus pentasulphide and (oxy) thionyl chloride does not yield the thio-thionyl chloride, as it is stated to do, but thionyl oxide, the chlorine, not the oxygen, going to the phosphorus. But there remains the work of Michaelis, of Thorpe, and of others; there is the very formation of the sulphurous ethers showing that the monochloride is the thiochloride of sulphur.

Prinz also records the results of several experiments made in the endeavour to replace the bivalent sulphur of the chloride by oxygen. These experiments were made by treating the thio-thionyl chloride with various oxides, and the result obtained was either negative, or else the oxides were converted to chlorides, and the sulphur chloride to sulphur and sulphur dioxide. But this was only to be expected, on any theory of its constitution, since sulphur will take oxygen in exchange for chlorine whenever the oxide of another element is present, which itself allows of such exchange. As Michaelis and Schifferdecker have shown, sulphur tetrachloride resembles phosphorous pentachloride in its property of exchanging chlorine for oxygen.

In saying, as Prinz does rightly enough, that thio-thionyl chloride behaves in some reactions like a mixture of sulphur with its tetrachloride, and in objecting for this reason to the view that it is the analogue of (oxy)thionyl chloride, he does not seem to have considered that this thionyl chloride itself—as he himself has pointed out—behaves sometimes as if it were a mixture of sulphur dioxide with sulphur tetrachloride:—



Ethyl Potassium Thionite.—This is Warlitz's salt with the constitution usually attributed to it, which appears to be the correct one. It stands apparently alone, and in this respect is of particular interest, as a metaloxyl compound of thionyl.

Nitrites—no Evidence that they are Oxylic.

As in the case of sulphites, two views have been held concerning the constitution of nitrites, as expressed by the formulæ $\text{Ag}.\text{NO}_2$ and $\text{AgO}.\text{NO}$. The former was suggested by Odling to the Society, many years ago, as probably the correct one, but the latter is now held by him, and, perhaps, universally by chemists.

I feel compelled, as I have stated in a paper read before the Society in 1883, entitled "On the Production of Hydroxylamine from Nitric Acid" (Trans., 1883, 443), to go back to that view of the constitution of nitrites in which they are represented as haloid or non-oxylic salts, and I now proceed to submit my argument, beginning, as in the case of sulphites, by endeavouring to show that there are no grounds to be found in the properties of nitrites for preferring an oxylic constitution for them. Such notions as the following have led to their being regarded as oxylic salts;—that all oxygenous salts are oxylic; that, because organic nitro-bodies are much more stable under certain conditions than metallic nitrites, they must be differently constituted; that the relations between nitrites and their organic derivatives appear simpler when nitrites are treated as oxylic than when they are treated as haloid or non-oxylic; and that the element nitrogen cannot be in direct union with metallic elements in saline combinations, above all if these contain oxygen.

Combined nitrogen unites directly with metallic elements, even in the presence of water, and even in the presence of oxygen in the reacting compounds; and at high temperatures displaces oxygen already combined with metals.—Ammonia acts on some metallic oxides and hydroxides, and on some oxygen salts, to form compounds—and that, too, not only in the case of the silver-mercury class of metals—in consequence of the metal rejecting oxygen for nitrogen.

The metallic "cyanates" can exist in solution, and they contain both oxygen and nitrogen, and yet there are probably not two opinions as to their being carbosylamines,* that is, so constituted as

* I venture to call attention to the advantage of substituting, as I have done in the text, the word "carbosyl" for "carboxyl," not so much because its sound is softer, as that it admits of the syllable "thio-" being prefixed to it to form a name for the analogous sulphur radicle, which "carboxyl" of course does not: thus we

to have nitrogen, and not oxygen, joining the metal to the carbon, thus: $O:C:N.Ag$. To this fact may be appended the consideration that since there are two series of hydrocarbon derivatives of the radicle oxycyanogen and two of the radicle nitrogen dioxide, the one having the hydrocarbon joined to the nitrogen, and the other having it joined to the oxygen, and since the oxycyanogen compounds of the metals are like the more stable series, in which the hydrocarbon is not united to the oxygen, it ought surely to be the case that the more stable nitro-hydrocarbons, in which the carbon is again not united to the oxygen, are the analogues of the metallic nitrites.

In the metallic ureas, we find metal in combination with the nitrogen, instead of with the oxygen of the urea. The reaction of mercury oxide on a solution of thio-urea is strikingly in point as to the preference of some metals for nitrogen, although here we have to do with sulphur instead of oxygen:—



The mercury, it is true, gets the sulphur, but not at once, for if it did, we should be left with urea, and that would certainly not become cyanamide. Instead of this, the mercury unites with the nitrogen and displaces the hydrogen, which with the oxygen of the metallic oxide forms the water, and then the mercury thio-urea breaks up into the simpler cyanamide and mercury sulphide.

Cyanamide forms salts, even in water, in which the metal is united with nitrogen. Also, when calcium carbamate* is heated, calcium cyanamide, $Ca:N.C:N$, is formed by the calcium separating from the oxygen of the carbamate to unite with the nitrogen.

The simple metallic cyanides themselves appear much more like carbamines than like nitrils; they are poisonous, they oxidise to "cyanates" or carbosylamines, and they yield the organic carbamines in reactions in which the heat is not so great as necessarily to convert these into nitrils. Hydrogen cyanide, too, is related to the

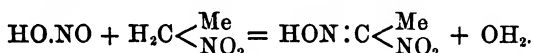
get "thiocarbosylamine." [Dr. Divers appears to be under a misapprehension in terming the radicle CO carboxyl, a name which is invariably given to the radicle $CO.OH$; the radicle CO , as is well known, is always termed carbonyl by English writers, and there does not seem to be any want of a new name. H. E. A.]

* Having mentioned this salt, I take the opportunity to claim some recognition of the part I had in its discovery. Drechsel now gets sole credit for this, but a reference to this Journal, 23, 230 and 361—363, will show that I, long before he had published his work, had pointed out the existence of this salt, and the effect of ammonia in preserving carbamates from decomposition, and had given a quantitative analysis of the calcium carbamate in combination with calcium chloride, a combination since examined by him, at least its analogue, the barium salt. In thus asking that my work may not be altogether ignored, I have no thought of denying to Drechsel the credit of his, so much more extended and exact than the incidental work of mine in this direction.

carbamines by its characteristic odour as well as by its poisonous quality; and since every carbamine yields formic acid when hydrolysed, the production of this acid from hydrogen cyanide does not make the latter a formyl compound, as usually represented, any more than it does any other carbamine. Cyanides being carbamines, why may we not, on the evidence of facts, write similar formulæ for two such similar salts as nitrite and cyanide of potassium?

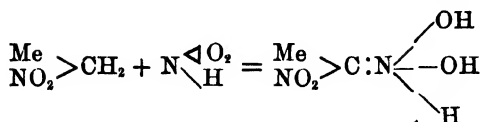
Nitrite.... $\text{K.N}:(\text{O}_2)''$. Cyanide.... $\text{K.N}:\text{C}''$.

The production of organo-nitroso-compounds is in no case of a kind to favour the oxylic theory of the constitution of nitrites.—The mode of formation of the nitro-paraffins, by both Kolbe's and V. Meyer's methods, clearly favours the view that the nitrogen of nitrites is united with the metal, but the formation of the nitrolic acids may seem to be unfavourable to it. Yet this is not the case. Although, when the formation is formulated as usual, and after V. Meyer—

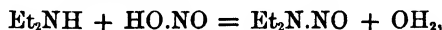


there seems to be a very simple cutting out of the oxygen and hydrogen to form water, and coming together of the bivalent organic residue and hydroxide, yet on consideration the appearance of simplicity will be seen to conceal intermediate changes which must occur. And when we do consider these, it will be found that the formula H.NO_2 is more in accordance with accepted views of this mode of elimination of the elements of water, as I shall proceed to show.

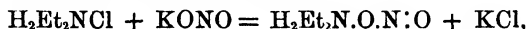
A body with the constitution HONO should form water by exchanging NO for hydrogen, as, according to wide experience, hydrocarbon hydrogen takes hydroxyl in preference to non-hydrogenised oxygen. Here I may recall, as in point, what I drew attention to in my former paper, that Lössen's method of obtaining hydroxylamine from ethyl nitrate, shows that it is not the hydroxyl of nitric acid even, that on reduction becomes the hydroxyl of the hydroxylamine, since the hydroxyl of the nitric acid (ethoxyl of the ethyl nitrate) is the first to be removed by the reducing process. But to continue. With the formula H.NO_2 the introduction of the hydroxide into the nitroethane is shown to proceed in the regular way; the oxygen atoms of the nitrite become hydroxyls; one of them along with the nitrite-hydrogen breaks off to form water; and the residual hydroxide and the nitroethane residue unite as required to form the nitrolic acid:—



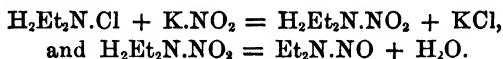
So, too, I think, with the formation of the nitrosamines, is it clear, that the non-oxylic constitution of the nitrites affords a satisfactory interpretation of the change, whilst the oxylic constitution does not, in spite of appearing to do so. Chemists now write—



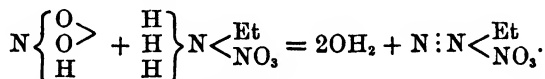
and the matter looks simple enough. But if we would represent the substances that actually must be used in order for the desired reaction to proceed, we have to write—



and then, only by some change of an “intramolecular” kind, that is, by a change which we do not see our way to represent rationally, can the diethylammonium nitrite become diethylnitrosamine and water. Now no such objection can be brought against the following equations, so far as I can see :—



The production of the diazoammonium or diazotammonium salts can be explained equally well by using either formula for the nitrite. With the new formula, the equation may be set out thus :—



Metallic nitrites are oxidisable, and therefore unlike organo-nitroxy-bodies, because of the presence in them of unoxidised metal.—Potassium nitrite, like potassium sulphite, is oxidisable for the reason that potassium is oxidisable. The instability of silver nitrite is of a different kind; like silver sulphite, it is not simply oxidisable, and, again like the sulphite, it is unstable by first decomposing so as to yield metallic silver as one of the products. Nitroethane is not oxidisable, because ethyl is not so. Its decomposition when heated with water and hydrochloric acid, in which the ethyl is changed, is due, of course, to interaction of the nitroxyl with the ethyl.

If Nitrites are not wholly Oxylic, then it is not true that all Oxygenous Salts are Oxylic.

Action of Phosphorus Oxychloride on Nitrites.—I have tried (again with the assistance of Mr. Shimidzu) the behaviour of silver nitrite

towards phosphorus oxychloride. There is considerable reaction, but in no case could we detect an oxychloride of nitrogen among the products. Nor did we succeed, even when we took more than twelve molecules of nitrite to one of the phosphorus compound, in preventing some of the latter from distilling over unchanged, leaving behind unchanged nitrite through which it had passed for a thickness of several centimetres. In the residue were silver chloride and phosphate, with unchanged silver nitrite. Volatilised were phosphorus oxychloride unchanged, and the third oxide of nitrogen, this being condensable by a freezing mixture to a green liquid containing a very little phosphorus oxychloride. The absence of oxychlorides of nitrogen may perhaps be accounted for by the fact, observed by Exner, that nitroxyl chloride is decomposed by silver nitrite, as no doubt would also be nitrosyl chloride if formed.

As the crucial test for the presence of oxylic oxygen, therefore, the action of phosphorus oxychloride fails in this case, no oxychloride of nitrogen being obtained. The production of the third oxide of nitrogen is, indeed, quite in accordance with the view of the oxylic structure of nitrites, but it is in no way decisive. The decomposition of silver nitrite by a gentle heat into silver, silver nitrate, and different oxides of nitrogen, is, as I have already shown in a former paper, so ready,* that, considering the imperfect action of phosphorus oxychloride on the silver nitrite, the results obtained are not remarkable on the view that the nitrites are non-oxylic salts. Indeed, it is difficult to see what simple reaction, with this constitution, could occur between the two compounds, or even how any reaction at all could happen were no traces of water or nitrate present in the nitrite. I believe pure and dry nitrites would be unaffected by pure phosphorus oxychloride.

The indication afforded by Exner's reaction between nitroxyl chloride and silver nitrite, depends on the view taken of the constitution of the fourth oxide of nitrogen.

Nitrites—Evidence that they have not an Oxylic Constitution.

The Quinine Test.—Silver nitrite at once destroys the fluorescence of a sulphuric acid solution of quinine. Other nitrites are less satisfactory, because of their entire decomposition by the acid.

Behaviour of the Silver Class of Metals and their Nitrites towards Nitric Acid.—The metals of the silver-mercury class never displace hydrogen from its combinations with oxygen. This fact comes out as clearly in the case of nitric acid as with any other hydroxyl-compound.

* This Journal, 24, 85. In some preliminary experiments by Mr. Shimidzu and myself, silver nitrite in a vacuum gave off at a gentle heat the second oxide of nitrogen almost pure, probably by reaction between NO_2 and AgNO_2 .

This being so, in order to account for the production of silver nitrate from nitric acid and silver, I made (in a former paper already referred to) what appears to me still the only appropriate assumption, namely, that in the first place silver nitrite and silver hydroxide are formed as transition-bodies, thus:— $2\text{Ag} + \text{HONO}_2 = \text{HOAg} + \text{AgNO}_2$, these afterwards being converted to nitrate by more nitric acid. In doing this, however, I had overlooked the striking results obtained by Russell, and presented by him to the Society in a paper entitled “On the Action of Hydrogen on Silver Nitrate.” Silver in dissolving in ordinary nitric acid actually does so as nitrite, but not also as hydroxide, for it dissolves only in nitric acid in the presence of a lower oxide or acid of nitrogen, a fact making the assumed formation of hydroxide unnecessary. I have to thank Dr. Armstrong for calling my attention to Russell’s work, which I find of special value in connection with my present object. Indeed, this work gives practically all the facts I have to bring forward in direct support of the view that nitrites are non-oxylic salts.

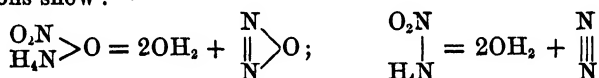
We have in Russell’s experiments proof, as nearly as possible, that silver, which cannot separate hydrogen from oxygen, separates it from nitrogen, and aided by this hydrogen then also dissolves in nitric acid itself, thus:— $2\text{Ag} + \text{HNO}_3 + \text{HONO}_2 = 2\text{AgNO}_2 + \text{H}_2\text{O}$. From this it would seem that nitrites must be non-oxylic, and thus different from nitrates. This explanation and equation, which I offered as a suggestion in my previous paper, to account for the much greater solvent power on silver of red nitric acid than that of the colourless acid, admits, however, of a modification, one which is greater in appearance than in reality. Nitrous acid has only a doubtful existence ever, and may not have one at all, even in presence of nitric acid. But then N_2O_4 will be there, and that is the same as dehydrated nitric and nitrous acids together; then $2\text{Ag} + (\text{NO}_2)_2 = 2\text{AgNO}_2$, and silver is seen uniting directly with nitrogen, when unable to decompose the oxylic compound, nitric acid.

Russell’s paper furnishes other evidence of the haloïd nature of nitrites. It is there pointed out that during the dissolution of silver in nitric acid, silver nitrite is formed in quantity, partly in solution in the silver nitrate liquor, partly as crystals. Its presence in solution is important, as showing that it is not the sparing solubility of the nitrite which causes its formation as insoluble matter. Now, if silver nitrite is an oxylic salt like the nitrate, this existence of silver nitrite in presence of nitric acid is as difficult to account for as its formation, for nitrites are ordinarily decomposable by the weakest acids. As a haloïd salt, the reason of its ability to exist in nitric acid is clear: silver tends to separate from oxygen, and *combines much more stably with nitrogen than with oxygen.*

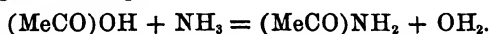
I have tested this matter in another way, by treating silver nitrite with dilute nitric acid and with dilute sulphuric acid. The nitrite dissolves without either colour or effervescence, and from the solution alkalis precipitate it unchanged. When potassium or sodium nitrite is similarly treated, it effervesces like a carbonate and gives a coloured solution and gas, the reason for this difference being that potassium is unstably combined with nitrogen in presence of oxygen, or of an oxygen-compound—it is of the zinc-tin class of metals.

Again indebted to Russell, I have to point out that whilst silver nitrate in solution is converted by free hydrogen to silver and nitric acid, silver nitrite is wholly unaffected by this gas. There is no accounting for this fact, so long as both salts are regarded as oxylic, the true explanation no doubt being that hydrogen separates silver from oxygen, and cannot separate it from nitrogen.

Heat-decomposition of Ammonium Nitrate and Nitrite.—The decomposition of ammonium nitrate into water and nitrous oxide, and that of the nitrite into water and nitrogen, seem in marked agreement with the theory that the one salt is oxylic and the other not, as the following equations show:—



But I would remark that, for these decompositions to be regarded as positively favourable to the theory, they must be essentially different in nature from those which takes place when ammonium salts of other acids become amides. In these, dissociation into acid and ammonia must precede the formation of water and the amide* by a reaction like the following, for example:—



It is probable enough, however, that the decomposition of the nitrate and nitrite is in reality different from that of most ammonium salts, in consequence of the readiness with which nitroxyl becomes deoxidised.

Nitrites being Non-oxylic, there is no Evidence that Nitrogen is ever Quinquevalent towards Oxygen.

Nitrates and nitrites having the same radicle NO_2 , there is not a single fact to support the notion that nitrogen is ever quinquevalent

* Or, as I showed in 1870 in my paper "On the Combinations of Carbonic Anhydride with Ammonia and Water," free ammonia must be made to act on the ammonium salt. In this case, the ammonium being bound in oxylic combination with the acid radicle, the free ammonia attacks the oxygen of the ammonoxyl, forming amide and water, and thus setting free by its own destruction another molecule of ammonia to take its place.

towards oxygen, as in nitrate compounds.* Nitrogen is, indeed, quinquivalent in ammonium and oxyammonium (including sulphazo) salts, and therefore may be so in other compounds, but the nitrogen of or in ammonium salts is no more capable of oxidation by ordinary laboratory reagents than free nitrogen, and nothing but active oxygen or plant-life seems capable of oxidising it.

The Double Atom of Oxygen as a Radicle.—The formation of nitrates in this way favours the notion of the nitrogen being united to a double atom of oxygen; and certainly the assumption that this is the case makes the chemistry of nitrate derivatives more easily intelligible. The non-existence of $\text{ON}(\text{OH})_3$, and of ONCl_3 , becomes a matter of course; so does the derivation of nitro-organic compounds, now from nitrate and now from nitrite, whilst the easy reducibility of these compounds to amides has already caused some chemists to write the radicle of nitrobenzene, for example: $-\text{N} \triangleleft \text{O}_2$, instead of $-\text{N} \begin{smallmatrix} \text{O} \\ \parallel \\ \text{O} \end{smallmatrix}$. That this double atom of oxygen is not so stable in nitroxyl compounds as it is in sulphuryl compounds seems due to the much weaker combination existing between nitrogen and oxygen than between sulphur and oxygen.

The quinquivalency of phosphorus to oxygen being so well established, and the periodic relations of the elements so certain, it is of moment to point out in connection with the tervalency of nitrogen to oxygen here deduced, that in the odd series the members of Group V are distinguished by an alternate rise and fall in degree of stable valency. Thus, nitrogen and arsenic pentachlorides are unknown, whilst those of phosphorus and antimony exist; nitric acid and arsenic acid readily yield oxygen, whilst phosphoric acid and antimonious acid are much more difficult to deoxidise. This alternation is not confined to Group V, but extends to the whole series, chlorine and iodine forming higher oxides than fluorine and bromine, sulphur and tellurium higher than oxygen and selenium.

Nitroxyl and Nitrosyl Compounds.—The radicle $-\text{NO}_2$ being the same whether it comes from nitrites or from nitrates, organo-nitro-bodies are evidently true organic nitrites, whilst the nitrous ethers are not, but in reality oxylic compounds of nitrosyl. As such they might be well called *nitrosites*. The only sources of these ethers are compounds of nitrosyl, principally the third oxide of nitrogen. Of

* It is stated in my paper on Hydroxylamine, that the chemical equation used therein to express the reduction of nitrate to nitrite is of interest "in representing the nitrogen as undergoing no change in quantivalence." My meaning has been somewhat misunderstood, and I see that I ought to have written, "in not representing the nitrogen as undergoing any change in quantivalence;" for it is in this respect that it differs from the equations usually given.

the existence of free nitrous acid there is simply nothing known. The formation of nitrous ether simultaneously with the true nitrites or nitroethane by the reaction between ethyl iodide and silver nitrite, may be considered as due to a secondary effect produced by the heat of the first change. The nitroethane is thus transformed to nitrous ether by the occurrence of a first step in that change which so readily proceeds, in which the nitroethane becomes acetic acid and hydroxylamine (V. Meyer), thus :—

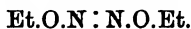
(1.) Dry nitroethane... $C_2H_5NO_2 = C_2H_5ONO$.

(2.) With water and acid $C_2H_5.ONO + OH_2 = C_2H_4O_2 + H_2NOH$.

The relative stability of nitroethane and nitrous ether depends, of course, on circumstances; under the condition of raised temperature, the nitrous ether is the more stable; in the presence of water, the nitroethane is the more so.

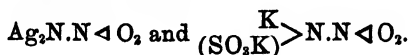
Too little is definitely understood concerning the constitution of the oxides of nitrogen to allow of the actual passage of nitrosyl compounds to nitroxyl compounds being profitably discussed at present. It will therefore suffice to point out that the formation of a metallic nitrite from the third oxide of nitrogen and a base, differs from the formation of an ethylic nitrosite from the same oxide and an alcohol, in being a case of oxidation of an acid radicle similar to the action of a base on chlorine or other acid radicle, and indeed on sulphur dioxide as sulphuryl.

Hyponitrites and Sulphuric Hyponitrites.—In connection with the theory here maintained, as to the non-oxylic character of unsaturated oxygenous salts, something must be said of hyponitrites and the nitrous radicle of sulphuric hyponitrites or nitrososulphates. That hyponitrites are non-oxylic I believe to be certain, but at present I am not prepared to say more. Zorn has proved that hyponitrites are bibasic, and that ethyl hyponitrite is not what I call an oxylic ether, although he writes this ether (somewhat inconsistently)



Had it this oxylic structure it would readily decompose with potassium hydroxide, and this, according to him, it does not do, even in presence of alcohol. Hyponitrites can be written as non-oxylic by giving them

a radicle, $\begin{array}{c} \text{—N—O} \\ | \quad | \\ \text{—N—O} \end{array}$, or preferably, $\text{—N—N} \triangleleft O_2$, having in either case the double atom of oxygen, thus :—



These formulæ are here given only as possibilities.

The Lower Acid Oxides are not true Anhydrides.

Sulphur dioxide and nitrogen trioxide are the anhydrides of the thionyl and nitrosic ethers, but they are not the anhydrides of sulphites and nitrites, if this term is used strictly. In uniting with basic oxides, they function like chlorine, as acid radicles. In confirmation of the truth of this conception of their nature, the recent researches of Reinitzer (*Ber.*, 14, 1886) may be mentioned. This chemist has shown that phosphorus trioxide does not appear to be the anhydride of the phosphites.

 XXXI.—*The Illuminating Power of Hydrocarbons.*

By PERCY F. FRANKLAND, Ph.D., B.Sc., Associate of the Royal School of Mines.

I.—*Ethane and Propane.*

FOR some time past I have been engaged in determining the illuminating power of those hydrocarbons which are either known or supposed to be present in coal-gas, and it was my intention to postpone the publication of the results until I had collected sufficient materials to establish the relationship which exists between illuminating power and chemical composition. In consequence, however, of the subject having been recently taken up by Mr. Lewis T. Wright, I feel myself compelled to publish, without further delay, some of the results which I have already obtained, and also to indicate more clearly than I have perhaps hitherto done, that I desire to continue the elaboration of these points which are the natural sequence of the investigations on illuminating power I have already communicated to this Society.

Since ethylene and benzene are the hydrocarbons to which the illuminating power of coal-gas is chiefly ascribed, these hydrocarbons were first submitted to examination. In a previous communication I had shown that the illuminating power of ethylene, calculated for a consumption of 5 cubic feet per hour from a "Referee's" burner, is 68.5 candles, and that of benzene under similar conditions is indirectly estimated to be six times as great.

The hydrocarbons, the investigation of which would naturally follow, are the paraffins. The first member of this series, methane, which constitutes about 40 per cent. of the volume of ordinary coal-

gas, was formerly supposed to yield practically no luminous effect, and that it might be replaced by hydrogen without impairing the illuminating power. The experiments upon which this opinion was based were made with the old fish-tail burner, and it was not until my experiments, in which the "Referee's" argand burner was employed, that the greater value of methane became apparent, and that methane itself was found to possess a low but very appreciable illuminating power.

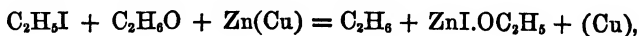
I have since determined the illuminating power of the second and third terms of the paraffin series of hydrocarbons, viz., ethane, C_2H_6 , and propane, C_3H_8 .

Ethane, C_2H_6 .

Preparation.—The method of preparation was essentially the same as that given by Gladstone and Tribe (*Trans.*, 1884, 154) for methane. A two-necked Woulff's bottle was filled with recently prepared zinc-copper couple, which had been repeatedly washed with methylated spirit (rectified over lime) to remove all water. One neck of the bottle was fitted with a dropping-funnel to admit of the introduction of ethylic iodide, whilst the other neck was fitted with a vertical tube about 2 feet long and 1 inch diameter, filled with closely packed zinc-copper couple washed with methylated spirit in the same way as the other; this tube acted as a scrubber, and was fitted at the top with a delivery-tube and also with a dropping-funnel, by means of which absolute alcohol could be admitted to moisten the surface of the zinc-copper couple.

The ethylic iodide was introduced into the Woulff's bottle in quantities of 20 c.c. at a time, and in every case mixed with an equal volume of absolute alcohol.

The reaction between the zinc-copper couple and the ethylic iodide, which may be represented by the equation—



only takes place very slowly at ordinary temperatures, so that it was found best to keep the Woulff's bottle partially immersed in water maintained at a temperature of $80^\circ C.$, when a regular stream of gas was evolved.

The gas, after traversing the zinc-copper scrubber, was made to pass through a bottle containing strong alcoholic soda before being collected in a gasholder filled with boiled water. The gas so collected was found to contain nearly 7 per cent. of ingredients soluble in fuming sulphuric acid, and this shows how wholly inadequate the zinc-copper scrubber is to purify the gas.

The gas was therefore made to pass in a slow stream through a wash-bottle containing bromine and water, then through another with caustic soda, and finally through an eprouvette filled with slaked lime. The gas thus purified was found, on analysis, to contain by volume—

	I.	II.
Gas absorbed by fuming sulphuric acid..	0·09	—
Carbonic anhydride	0·22	—
Oxygen	0·46	—
Nitrogen	1·35	1·50
Combustible gas (ethane).....	97·88	97·73
	<hr/> 100·00	

One volume of the “combustible gas” yielded on explosion with excess of oxygen—

	I.	II.
Contraction	2·493	2·498 vols.
Carbonic anhydride.....	1·993	1·991 „
Oxygen used	3·517	3·519 „

Thus corresponding closely with the figures required for ethane, which yields on explosion—

Contraction	2·5 vols.
Carbonic anhydride.....	2·0 „
Oxygen used	3·5 „

Illuminating Power.—The gas was consumed from a “Referee’s” burner, and the photometric determination made by comparison, both with standard candles and with the Methven standard, the mean of ten observations being taken in each case.

Experiment.	Candles observed.	Rate.		Illuminating power corrected to 5 cubic feet of gas and 120 grains of spermaceti per hour. Temp. 60° F. Pressure 30 in.
		Gas in cubic feet per hour.	Candles in grains per hour.	
I	14·3	2·14*	117·7	33·23 candles.
II	15·8	2·08	120·0	38·47 „
III	16·2	1·97	105·6	35·75 „
IV (Methven)	11·9	1·82	—	32·51 „
				<hr/> 4 139·96 „
				Mean. 34·99 „

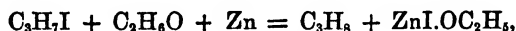
* In this experiment the rate of consumption was by accident taken for one revolution of the meter only.

From the mean of the above four photometric determinations, the illuminating power of ethane is found to be 85 candles. I have already shown (Trans, 1884, p. 227) that the illuminating power of ethylene is 68·5 candles, or almost double that now found for ethane. Thus the two hydrocarbons, ethane, C_2H_6 , and ethylene, C_2H_4 , differing as they do only in the matter of two atoms of hydrogen, yet exhibit this marked disparity in their illuminating power.

Propane, C_3H_8 .

Preparation.—As the action of the zinc-copper couple on isopropyl iodide is inconveniently violent, it was deemed advisable to employ granulated zinc instead. The apparatus used was exactly the same as that already described for the preparation of ethane, only that the zinc-copper couple in the generating vessel was replaced by granulated zinc which had been cleaned with dilute sulphuric acid, and then well washed with rectified methylated spirit. The zinc-copper couple was, however, retained in the scrubber, since the greater activity of the couple would tend to decompose the vapour of isopropyl iodide more perfectly.

The isopropyl iodide was in all cases added along with an equal volume of absolute alcohol. The evolution of gas according to the equation—



takes place only very slowly in the cold, but on immersing the generating vessel in hot water it is almost inconveniently rapid. The gas was passed in succession through alcoholic soda, bromine, and water, a strong solution of caustic soda, and an eprouvette filled with slaked lime. On analysis, however, it was found that the gas contained about 2 per cent. of ingredients soluble in fuming sulphuric acid, and it was therefore again passed in a slow stream through the same purifying apparatus, omitting only the alcoholic soda. The proportion of gas soluble in fuming sulphuric acid was not very materially diminished, and as a certain amount of air is unavoidably introduced by each successive process of purification, the photometric examination was at once proceeded with.

The gas, after the second purification, was found on analysis to have the following composition:—

100 volumes of gas contained—

	I.	II.
Carbonic anhydride	0·30	1·99
Oxygen	1·68	
Nitrogen	3·02	
Combustible gas (propane)	95·00	
	<hr/> 100·00	<hr/> 100·00

One volume of the combustible gas yielded on explosion with excess of oxygen—

	I.	II.
Contraction	3·009	3·022 vols.
Carbonic anhydride	2·981	2·960 „
Oxygen used	5·030	5·026 „

Thus corresponding with the figures required for propane, which yields on explosion—

Contraction.....	3·00 volumes.
Carbonic anhydride	3·00 „
Oxygen used.....	5·00 „

Illuminating Power.—The photometric determinations were made, as before described, both standard candles and the Methven standard being used for comparison. The mean of ten observations being taken in each case :—

Experiment.	Candles observed.	Rate.		Illuminating power corrected to 5 cubic feet of gas and 120 grains of spermaceti per hour. Temp 60° F. Pressure 30 in.
		Gas in cubic feet per hour.	Candles in grains per hour.	
I.....	16·36	1·62	122·4	51·71 candles.
II (Methven)	14·12	1·27	—	56·11 „
				2 107·82 „
				Mean. 53·91 „

These results show that the illuminating power of propane is almost exactly 1·5 times as great as that of ethane: thus $35 \times 1·5 = 52·5$ candles.

This difference in their luminiferous value is in perfect accord with the difference in their chemical composition, propane containing 1·5 as many atoms of carbon as ethane.

It is only reasonable to anticipate that the illuminating power of butane, C_4H_{10} , with the investigation of which I am at present engaged, will be found to be twice as great as that of ethane, or, in other words, equal to that of ethylene.

I am also at present engaged in determining the illuminating power of the members of other series of hydrocarbons, and hope before long to be able to communicate further results.

The results which I have thus far obtained may be briefly summarised :—

The illuminating power of ethane is 35 candles, or half that of ethylene.

2. The illuminating power of propane is 54 candles, or 1.5 times that of ethane.

3. In the paraffin series of hydrocarbons, excluding the first member, methane, the illuminating power appears to be directly proportional to the number of carbon-atoms in the molecule. It remains, however, to be seen whether the higher members of the series also conform to the law which holds good in the case of ethane and propane.

XXXII.—*Benzoylacetic Acid and some of its Derivatives.* Part II.

By W. H. PERKIN, Jun., Ph.D., Privatdocent at the University of Munich.

IN Part I of this research (Trans., 1884, 170), I described the preparation and properties of ethylic benzoylacetate and of benzoylacetic acid, as well as of some compounds in which the hydrogen-atoms of the methylene group of the former are displaced by alcoholic radicles, such as ethyl-, diethyl-, and allyl-benzoylacetic ether, together with the products of their hydrolysis. Before describing the more complicated reactions in which ethylic benzoylacetate takes part, I should like to give the results of the experiments I have made with some of these compounds since the publication of Part I (Trans., 1884, 170).

It has been found that although the substituted etheric salts of the benzoylacetic acids cannot be distilled without decomposition under the ordinary pressure, they can easily be obtained pure by distillation under diminished pressure. Using an apparatus similar to that described by Thorne, I have succeeded in purifying the monethyl- and allyl-derivatives described in the previous paper. If the crude product of the action of ethyl iodide on ethylic benzoylacetate is distilled under a pressure of 225 mm., a small quantity of acetophenone passes over first, and then the temperature rises rapidly to 220°, between which and 240° nearly the whole comes over as an almost colourless oil, leaving but a small residue. On repeatedly refractioning this oil under the same pressure, it distils mostly between 230—235°. The portion used for analysis boiled at 231—232° at 225 mm.

0.1550 gram substance gave 0.1020 gram H_2O and 0.4016 gram CO_2 .

	Found.	Theory. $C_6H_5 \cdot CO \cdot CH(C_2H_5) \cdot COOC_2H_5$.
C	70·66 per cent.	70·91 per cent.
H	7·31 "	7·27 "
O	22·03 "	21·82 "

Ethyllic ethylbenzoylacetate is a colourless, strongly refracting oil possessing an aromatic odour and burning taste. When pure, it appears to distil at the ordinary pressure almost without decomposition. The boiling points of the pure substance were incidentally noticed as being—

210—211°	at	90 mm.
223—224	"	150 "
231—232	"	225 "

Ethyllic ethylbenzoylacetate is insoluble in potassic hydroxide solution, but appears to give a sodium compound on mixing it with sodic ethoxide. On continued boiling, no condensation-product is formed corresponding with the dehydrobenzoylactic acid, which is so easily obtained by heating ethyllic benzoylacetate for a short time by itself. This reaction I hope to describe in Part III of this paper. Ethyllic acetoacetate and ethylacetoacetate behave in a precisely similar way. On passing ethyllic acetoacetate through a tube at a dull red heat, it is almost completely decomposed, yielding as much as 20 per cent. of its condensation-product, dehydracetic acid, whereas ethyllic ethylacetoacetate passes through almost unaltered, no trace of the analogous acid being formed.

Ethyllic allylbenzoylacetate may also be purified in exactly the same way as ethyllic ethylbenzoylacetate. On submitting the crude product of the action of allyl iodide on ethyllic benzoylsodacetate to distillation under a pressure of 225 mm., nearly the whole passes over between 225—245° as a peculiar greenish-coloured oil, with a slight reddish fluorescence. This coloration can only be removed by repeated fractioning, and even then it often returns on standing.

Pure ethyllic allylbenzoylacetate boils at—

220°	under	100 mm. pressure.
226—227°	"	130 "
240—241	"	225 "

As it is difficult to burn, it is necessary that the combustion should be done with chromate of lead. The following numbers were obtained :—

0·1491 gram substance gave 0·0902 gram H_2O and 0·3924 gram CO_2 .

	Found.	Theory. $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}(\text{CH}_2\cdot\text{CH}_2\cdot)\cdot\text{COOC}_2\text{H}_5$.
C	71.77 per cent.	72.41 per cent.
H	6.72 „	6.89 „
O	21.51 „	20.69 „

Ethylc allylbenzoylacetate possesses the peculiar disagreeable odour characteristic of most allyl compounds. It does not solidify at 0° . The solution in acetic acid takes up bromine readily, especially if warmed, and without evolution of hydrobromic acid.

Ethylc benzoylacetate itself cannot be purified by distillation under diminished pressure, the greater part being decomposed, owing to the comparative slowness with which distillation takes place. When distilled as rapidly as possible (at 200 mm.) a portion passes over between 220 — 225° , consisting of nearly pure ethylc benzoylacetate, but a large residue is left containing considerable quantities of dehydrobenzoylacetic acid.

Having obtained ethylc monethyl- and allyl-benzoylacetates in a pure state, it was next thought necessary to repeat the hydrolysis with potash, in order, if possible, to obtain the acids in a pure state, but even when very dilute alcoholic potash was used, the acids were always mixed with benzoic acid, in some cases to a very considerable extent.

It was then thought that hydrolysis with sulphuric acid might give better results, and several experiments were therefore tried, using ethylc benzoylacetate itself in the first case.

On mixing ethylc benzoylacetate with 20 times its volume of concentrated sulphuric acid, and allowing it to remain for some time, the mixture becomes thick and dark-coloured, small quantities of carbonic anhydride and sulphurous anhydride being given off.

After standing for 14 days, the product was poured into ice water; this caused the precipitation of a thick dark brownish oil, which partly solidified on prolonged agitation. This uninviting body was separated from the aqueous solution by filtration, washed well with water, and then spread out on a porous plate; in this way the dark brown oil was almost completely removed from the crystals in two or three days, leaving them as a hard yellowish crystalline crust. After recrystallising it several times from warm benzene, the substance was easily obtained pure, melting between 103 — 104° , and presenting all the appearance of benzoylacetic acid.

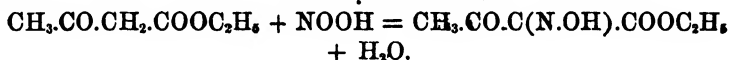
On adding a drop of ferric chloride to the alcoholic solution, it gave the beautiful violet coloration mentioned in Part I, and the acid itself on dry distillation split up quantitatively into carbonic anhydride and acetophenone. There can be no doubt, therefore, that the substance was pure benzoylacetic acid. Experiments were next tried

to ascertain if ethylic ethylbenzoylacetate could also be hydrolysed in the same way. A small quantity of this ethereal salt was mixed with nearly three times its volume of concentrated sulphuric acid, and allowed to remain for three weeks. The solution became brownish-coloured, but not nearly so dark as in the case of ethylic benzoylacetate itself; on adding water, an almost colourless oil was precipitated, which was removed by shaking with ether, and on evaporating the ether, a yellowish oil remained behind; this when exposed over sulphuric acid in a vacuum, deposited crystals, apparently ethylbenzoylacetic acid. The quantity, however, was unfortunately too small for analysis, so that it will be necessary to repeat the experiment with more material before I can be certain that this method is of general application for the hydrolysis of ethylic benzoylacetate derivatives.

Part II of this research comprises the preparation and properties of ethylic nitrosobenzoylacetate, dibenzoylacetic acid, di- and tri-benzoylmethane, the reduction of ethylic benzoylacetate, the action of phosphorous pentachloride on ethylic benzoylacetate, and the condensation of the latter with benzaldehyde.

Ethylic Benzoynitrosoacetate.

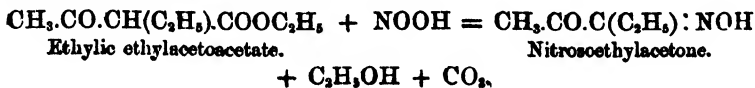
By the action of nitrous acid on ethylic acetoacetate, Victor Meyer obtained ethylic nitrosoacetoacetate, according to the equation—



After a series of admirable researches, he proved that the formula of this compound was not $\text{CH}_3\text{CO}\cdot\text{CH}(\text{NO})\text{COOC}_2\text{H}_5$, and therefore did not contain the nitroso-group NO, as was at first supposed, but that it was in reality an isonitroso-body, having the constitution $\text{CH}_3\text{CO}\cdot\text{C}(\text{N}\cdot\text{OH})\text{COOC}_2\text{H}_5$, and containing the isonitroso-radicle : N.OH.

With the exception of ethylic malonate, ethylic acetoacetate is the only compound which is capable of being converted into an isonitroso-derivative; for the substituted acetoacetates, such as ethylic ethylacetoacetate, $\text{CH}_3\text{CO}\cdot\text{CH}(\text{C}_2\text{H}_5)\text{COOC}_2\text{H}_5$, possessing only one hydrogen-atom which is capable of being substituted by any group, cannot combine with the dyad radicle NOH.

The nitroso-derivative of the whole molecule is therefore never formed by the action of nitrous acid on such bodies, but the ethereal salt being first hydrolysed, carbonic anhydride is given off, and the nitroso-ketone remains behind :—



It therefore appeared interesting to try the action of nitrous acid on ethylic benzoylacetate and some of its derivatives, in order to determine whether they would follow the same law or not.

After several trials, the following was found to be the best method of preparing ethylic nitrosobenzoylacetate:—

Ethylic benzoylacetate is first dissolved in dilute sodic hydroxide solution, filtered, mixed with an excess of sodic nitrite, and cooled down below 0° in a freezing mixture. Dilute sulphuric acid is then slowly added from a burette until the mixture is decidedly acid, care being taken that the liquid does not get warm. After a short time, more sodic hydroxide solution is added; this dissolves all that was precipitated by the sulphuric acid, producing an intense yellow solution, a sign that a nitroso-body has been formed. Last of all, the ethylic nitrosobenzoylacetate is precipitated by adding an excess of sulphuric acid. It separates as an oil, which, however, on agitating soon solidifies to long colourless needles. These are collected, well washed with water, and separated from any oily matter by spreading them out on a porous plate. In order to purify it, it is dissolved in a little hot alcohol, and water added until it becomes milky. The whole is then warmed up again and allowed to stand, when pure ethylic nitrosobenzoylacetate separates out in beautiful long colourless needles; on analysis, these gave the following numbers:—

- I. 0.1711 gram substance gave 0.0813 gram H_2O and 0.3729 CO_2 .
 II. 0.1566 gram substance gave 0.0730 gram H_2O and 0.3423 gram CO_2 .
 I. 0.2617 gram substance gave 16 c.c. N, bar. = 718 mm., $t. = 21^{\circ}$.
 II. 0.2154 " " 12.5 c.c. N, bar. = 716 mm., $t. = 18^{\circ}$.

	Found.		Theory. $C_{11}H_{11}NO_4$.
	I.	II.	
C	59.44	59.62 per cent.	59.73 per cent.
H	5.28	5.18 "	4.97 "
N	6.56	6.31 "	6.33 "
O	28.72	28.89 "	28.96 "

From its analogy to ethylic nitrosoacetoacetate, this compound must have the formula $C_6H_5.CO.C(N.OH).COOC_2H_5$.

Ethylic nitrosobenzoylacetate melts at $120-121^{\circ}$. It is easily soluble in alcohol, ether, benzene, and chloroform, sparingly in water. It dissolves easily in alkalis, forming a yellow solution like all nitroso-bodies, and on acidifying is reprecipitated unchanged. It is decomposed by dry distillation with separation of charcoal and formation

of hydrocyanic acid. A heavy oil passes over, which soon solidifies, and then melts at $110-114^{\circ}$; it is perhaps impure benzoic acid.

On treating ethylic nitrosoacetoacetate with alkalis, it is decomposed in the same way as ethylic acetoacetate itself, yielding nitrosoacetone instead of acetone. It was thought likely, therefore, that ethylic nitrosobenzoylacetate under the same conditions would give nitrosoacetophenone.

In order to test this, 3 grams of ethylic nitrosobenzoylacetate were dissolved in dilute potash, and allowed to remain for some days at the ordinary temperature, when the yellow solution of the nitroso-derivative became quite colourless. The product was then cooled in a freezing mixture, acidified with sulphuric acid, and extracted with ether. On evaporating the ethereal solution, it deposited a colourless crystalline substance, which contained but traces of nitrogen, and therefore could not be nitrosoacetophenone. It is easily soluble in warm water, and on cooling crystallises in small thick prisms, which were collected, dried over sulphuric acid in a vacuum, and analysed, with the following results:—

- I. 0.1797 gram substance gave 0.0684 gram H_2O and 0.3962 gram CO_2 .
 II. 0.1247 gram substance gave 0.0477 gram H_2O and 0.2747 gram CO_2 .

	Found.		Theory. $C_9H_8O_4$.
	I.	II.	
C	60.13	60.08 per cent.	60.00 per cent.
H	4.22	4.25 „	4.44 „
O	35.65	35.67 „	35.55 „

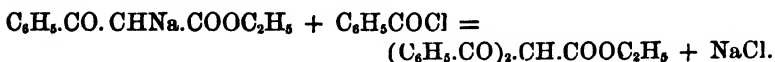
The compound therefore appears to have the formula $C_9H_8O_4$. It crystallises from water in small prisms melting at 125° . It dissolves easily in alkalis, forming a colourless solution. On precipitating the neutral solution of the ammonium salt with silver nitrate, the silver salt was obtained as a voluminous white precipitate, which after being dried over sulphuric acid in a vacuum gave the following numbers on analysis:—

0.3050 gram substance gave 0.1147 gram Ag = 37.61 per cent.
 Theory, $C_9H_7O_4Ag$ = 37.63 „

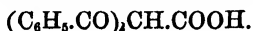
I hope at some future time to be able to examine more thoroughly this curious reaction, and if possible to determine the constitution of the body $C_9H_8O_4$.

Dibenzoylacetic Acid.

In the preceding chapters, it has been shown that ethylic benzoylacetate is capable of forming derivatives in which the hydrogen atoms of the methylene group are displaced by alcoholic radicles such as ethyl, allyl, &c., in exactly the same way as ethylic acetoacetate. It was thought likely that very interesting results might be obtained if the acid chlorides such as benzoyl chloride were substituted for the iodides of the alcoholic radicles in the above reaction. If the sodium compound of ethylic benzoylacetate be heated with benzoyl chloride, the ethyl salt of dibenzoylacetic acid is formed according to the equation—



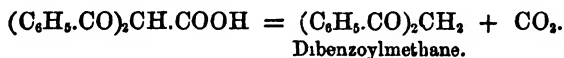
This ethereal salt on hydrolysis gives dibenzoylacetic acid,



When boiled with dilute acids, dibenzoylacetic acid is easily split up into acetophenone, benzoic acid, and carbonic anhydride, thus—



If boiled with water, a second reaction takes place at the same time, by which dibenzoylmethane is formed according to the equation—



In the preparation of ethylic dibenzoylacetate, it is not necessary to use the pure dry sodium compound of ethylic benzoylacetate and act on it with benzoyl chloride in ethereal solution, as was done in the first experiments, but we may proceed in the way usually employed in such syntheses, that is, by mixing ethylic benzoylacetate with sodic ethylate, and allowing benzoyl chloride to act directly on the product in the following way:—0.6 gram of sodium is dissolved in absolute alcohol, well cooled, and then mixed with 4 grams of ethylic benzoylacetate. 3 grams of benzoyl chloride are now added drop by drop, the whole being well cooled in a mixture of ice and salt. The reaction is very energetic, each drop of benzoyl chloride instantly producing a precipitate of chloride of sodium, and so much heat is developed that the alcohol will boil if a refrigerating mixture is not used. After all the benzoyl chloride has been added, the whole is warmed on a water-bath for about a quarter of an hour to insure the reaction being complete, and the greater part of the alcohol is distilled off; water is then added, and the product allowed to re-

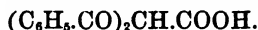
main for some time, in order to insure the decomposition of any slight excess of benzoyl chloride. The watery liquid is next extracted with ether once or twice, the ethereal solution well shaken with carbonate of soda to remove benzoic acid, dried over potassium carbonate, and the ether distilled off. A thick dark brown oil remains behind. This was not further purified, although it is possible that by fractioning in a vacuum the ethylic dibenzoylacetate might be obtained in a pure state, as in the case of the ethyl- and allyl-benzoyl-acetates.

In order to obtain the free acid, the crude ethereal salt was hydrolysed by warming with an excess of alcoholic potash for about ten minutes on a water-bath. The mixture became dark coloured, and on adding water almost all of it dissolved, forming a dark brownish solution; this when acidified deposited the crude dibenzoylacetic acid as a thick oil, which became nearly solid on agitating for a short time. The product was collected, well washed with water, and dissolved in as little boiling alcohol (80 per cent.) as possible. On cooling, the acid crystallised out in colourless nodules, and was easily obtained pure and free from benzoic acid by repeated crystallisation. On analysis the following numbers were obtained:—

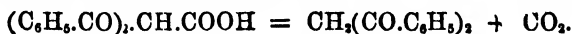
0.2257 gram substance gave 0.0925 gram H_2O and 0.5926 gram CO_2 .

	Found.	Calculated.
		$C_{16}H_{12}O_4$.
C	71.61 per cent.	71.64 per cent.
H	4.55 ,,	4.48 ,,
O	23.84 ,,	23.88 ,,

This substance was therefore dibenzoylacetic acid,



The acid melts at 109° . When rapidly heated in small quantities, some of it distils undecomposed, but the greater part is split up into dibenzoylmethane and carbonic anhydride according to the equation—



Dibenzoylacetic acid.

Dibenzoylmethane.

Dibenzoylacetic acid is sparingly soluble in water and cold alcohol, but easily so in hot alcohol, benzene, and ether. The solution in alcohol gives a dirty red coloration on the addition of ferric chloride. The acid dissolves in concentrated sulphuric acid, producing a yellow solution, which, however, becomes colourless on warming. It dissolves slowly in solutions of ammonia, sodic hydroxide, and sodic carbonate, and is reprecipitated on the addition of an acid. In order to obtain a neutral solution of the ammonium salt, the pure acid was

dissolved in a slight excess of dilute ammonia, and then allowed to stand over sulphuric acid in a vacuum until the excess of ammonia had evaporated. The salt itself is very easily soluble in water; on boiling the solution, carbonic anhydride is given off, and the smell of acetophenone becomes noticeable. Several of the salts of dibenzoylacetic acid were prepared by precipitating the solution of the ammonium salt with various reagents. The *silver salt* is obtained on adding a solution of nitrate of silver as a white curdy precipitate, sparingly soluble in water. For analysis, the substance was dried at 80°.

0.1154 gram substance gave 0.0327 gram silver.

	Found.	Theory.
		$(C_6H_5CO)_2CH.COOAg.$
Ag	28.34 per cent.	28.72 per cent.

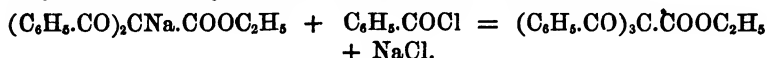
A solution of cupric sulphate precipitates the *copper salt* as a light yellowish-green mass, which appears to be somewhat soluble in hot water and alcohol. Prolonged boiling, however, decomposes the salt, cupric oxide being precipitated. This copper salt dissolves easily in ammonia, yielding a beautiful blue solution. The *barium salt* is soluble in water, and is prepared by shaking the finely powdered acid with baryta-water and a little alcohol for some time. After precipitating the excess of baryta by passing carbonic anhydride and filtering, a solution of the salt is obtained, which, however, is partly decomposed by evaporation. The *zinc salt* is also easily soluble in water. With a solution of the ammonium salt, acetate of lead gives a white curdy precipitate of the *lead salt*. With a solution of sulphate of nickel, the *nickel salt* is obtained as a light green precipitate soluble in excess of sulphate of nickel. Ferric chloride gives a brownish-red coloration with dilute solutions of the ammonium salt; with more concentrated solutions, however, the *ferric salt* is precipitated as a dirty reddish precipitate somewhat soluble in hot water. Ferrous sulphate gives the same reaction. Chloride of tin precipitates the *tin salt* as a heavy white mass sparingly soluble in water.

If dibenzoylacetic acid is mixed with alcoholic potash, a yellowish-green solution is formed which is decomposed by boiling, benzoic acid and a neutral body being formed. On distilling dibenzoylacetic acid with soda-lime, it is split up into benzene and an oily substance, which appears to be acetophenone.

In order to obtain pure ethylic dibenzoylacetate, the pure acid was dissolved in absolute alcohol, and hydrogen chloride passed through the solution until it was thoroughly saturated, the whole being kept well cooled during the operation. On adding water, an oil was precipitated, which, on distillation, came over almost entirely between

205—220° as a colourless oil smelling strongly of ethyl benzoate. The pure ether can easily be prepared, however, by decomposing the silver salt of the acid with ethylic iodide in ethereal solution. After filtering from the precipitated iodide of silver and evaporating on a water-bath, ethylic dibenzoylacetate remains behind as a thick colourless oil of a faint fruity odour; it does not solidify when cooled down to -10° .

Several experiments were next made in the hope of obtaining tribenzoylactic acid by treating ethylic dibenzoylacetate with sodic ethylate and benzoyl chloride as expressed in the equation—



In this way an almost colourless oil is obtained which, however, is unfortunately completely split up on hydrolysis, nothing but benzoic acid being formed.

As it appeared probable that ethylic tribenzoylacetate was really formed in the first place, an experiment was very carefully made with pure ethylic dibenzoylacetate, and the product freed from excess of benzoyl chloride and benzoic acid by shaking with dilute sodic carbonate was dried over carbonate of potash and analysed.

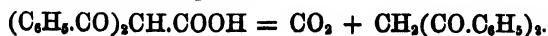
	Found.	Theory. (C ₆ H ₅ .CO) ₃ C.COOC ₂ H ₅ .	Theory (C ₆ H ₅ .CO) ₃ CH.COOC ₂ H ₅ .
C	74.19 per cent.	75.00	72.97 per cent.
H	4.91 ,,	5.00	5.41 ,,
O	21.00 ,,	20.00	21.62 ,,

This ethereal salt is a very thick yellowish oil, which unfortunately could not be made to crystallise. On boiling it with dilute sulphuric acid, acetophenone and a solid acid, probably benzoic acid, are formed. It dissolves in alcoholic potash and is reprecipitated on adding a few drops of water, whereas ethylic dibenzoylacetate is only precipitated from its solution in alcoholic potash on the addition of a much larger quantity of water.

DECOMPOSITION-PRODUCTS OF DIBENZOYLACETIC ACID.

Dibenzoylmethane.

As dibenzoylactic acid contains two carbonyl-groups, it seemed probable that interesting results might be obtained by carefully examining its decomposition-products. The acid was therefore treated with several reagents; first of all with dilute sulphuric acid in the hope of simply splitting off carbonic anhydride, and thus obtaining dibenzoylmethane according to the equation—



The experiment was carried out in the following way:—A mixture of pure dibenzoylacetic acid with an excess of dilute sulphuric acid (1 : 2) was heated for about five hours in a flask connected with a reflux condenser; at the end of this a test-tube containing baryta-water was fixed, to serve as a rough indicator both of the quantity of carbonic anhydride and the rate at which it was given off.

The acid soon began to decompose and swam about in the liquid at first as a semi-solid mass, but later on in large oily drops, a considerable quantity of carbonic anhydride being evolved. At the end of the reaction, the contents of the flask, which smelt strongly of acetophenone, were subjected to distillation by steam; in this way a considerable quantity of a colourless oil passed over and was extracted by shaking with ether. On distilling off the ether and subsequent fractioning, nearly the whole of the residual oil passed over between 195—205°, and without doubt consisted of nearly pure acetophenone. In order to be certain, it was shaken with a solution of orthonitrobenzaldehyde in dilute sodic hydroxide, when a considerable quantity of indigo was precipitated after the mixture had been standing for some time.

On cooling, the residue in the flask deposited a quantity of glittering crystals which were collected and dried. They melted at 120° and showed all the properties of benzoic acid, with which they were no doubt identical.

Dibenzoylacetic acid is therefore decomposed by boiling with dilute sulphuric acid into benzoic acid, carbonic anhydride, and acetophenone according to the equation—



In repeating this reaction more carefully, it was noticed that if the boiling with sulphuric acid were stopped before all the dibenzoylacetic acid had been decomposed, a small quantity of a solid body, insoluble in sodic carbonate, could be isolated; when this is dissolved in alcohol and ferric chloride added, it gives a beautiful reddish-violet coloration. As, however, only very small quantities of this compound could be obtained by this method, several experiments were tried in order to improve the yield, and it was found that simple boiling with distilled water gave the desired result.

Pure dibenzoylacetic acid was boiled with water in a flask connected with a reflux condenser as long as carbonic anhydride continued to come off in any quantity (about 4—5 hours).

The acid melted slowly and sank to the bottom of the flask as a heavy, slightly brownish oil which on cooling partially solidified, the liquid becoming filled with needles of benzoic acid. A dilute solution of sodic carbonate was now added, and the whole well

shaken and allowed to stand for some time until all the benzoic acid had dissolved. After filtering and washing with water a small quantity of a semi-solid mass remained, smelling strongly of acetophenone; the latter can be roughly separated from the crystals by spreading them out on a porous plate or by pressing between blotting-paper. The crude product thus obtained was then dissolved in a little hot methyl alcohol from which it crystallised on cooling in beautiful flat plates; these are easily obtained pure by recrystallisation.

The analysis gave numbers agreeing with the formula—



0.1967 gram substance gave 0.0952 gram H_2O and 0.5772 gram CO_2 .

	Found.	Calculated. $\text{CH}_2(\text{CO}.\text{C}_6\text{H}_5)_2.$
C	80.03 per cent.	80.36 per cent.
H	5.37 ,,	5.36 ,,
O	13.60 ,,	14.28 ,,

This compound was therefore dibenzoylmethane or benzoylacetophenone. It melts at 81° and distils above 200° apparently without the least decomposition. It is easily soluble in ether, alcohol, and chloroform, the alcoholic solution, on the addition of a drop of ferric chloride, giving an intense reddish-violet coloration which resembles very closely that produced by benzoylactic acid itself. If the solution in hot methyl alcohol is cooled slowly, it crystallises most beautifully; it can, however, best be obtained in large crystals by allowing the ethereal solution to evaporate slowly. Professor Hanshofer was kind enough to measure these crystals, and gave me the following description of them:—

Crystalline system rhombic:

$$a : b : c = ? : 1 : 1.38.$$

Small crystals with rhomboïdal base and extended in the direction of the makrodiagonal on which the surface $0P(c)$, $\infty P_\infty(a)$, $\bar{P}_\infty(r)$ and an undetermined makrodome, d , were observed. The only surfaces fit for measurement were a , r , and in some crystals c . The



surface *d* is smooth, curved, and appears only on one-half of the crystals (with respect to the basal section). The surface *c* is also generally curved.

	Measured.	Calculated.
<i>r</i> : <i>r</i>	108° 18'	—
<i>c</i> : <i>r</i>	125° 54'	125° 51'
<i>a</i> : <i>r</i>	90°	90°

The compound is remarkable by the strong dispersion in its axes. The medial line is the vertical axis. The makropinacoid is the plane of the optical axis for the red, and the brachypinacoid for the blue. In the polariscope with white light, the surface *c* shows the interference figure of rhombic titanite acid (brookite).

Dibenzoylmethane is easily soluble in alkalis, particularly in alcoholic potash, and is reprecipitated unchanged on acidifying. It combines easily with phenylhydrazine, forming a solid substance which, however, was not further examined.

Tribenzoylmethane.

Dibenzoylmethane, $\text{CH}_2(\text{CO.C}_6\text{H}_5)_2$, contains a methylene-group associated with two carbonyl-groups, and for this reason is soluble in alkalis, forming metallic salts, the methylene-group in this body behaving in exactly the same way as the corresponding one in ethylic benzoylacetate, $\text{C}_6\text{H}_5\text{CO.CH}_2\text{COOC}_2\text{H}_5$. It appeared probable, therefore, that by further treatment with sodic ethylate and benzoyl chloride a tribenzoylmethane might be formed according to the equation—



This is in reality the case, as will be seen from the following experiment: 2 grams of pure dibenzoylmethane were mixed with a solution of 0.2 gram of sodium in absolute alcohol, and then as soon as all had completely dissolved 1.4 gram of benzoyl chloride was added drop by drop. Sodic chloride was immediately precipitated, the mixture becoming warm. After all the benzoyl chloride had been added, the product was heated on a water-bath for about ten minutes to ensure the reaction being complete; a quantity of water was then added, when a solid body separated; this was collected, well washed with water, and spread out on a porous plate to remove a small quantity of oil adhering to the crystals.

The compound was easily purified by recrystallisation from alcohol, and gave the following numbers on analysis:—

0.1849 gram substance gave 0.0864 gram H_2O and 0.5443 gram CO_2 .

	Found.	Theory. $\text{CH}(\text{CO}.\text{C}_6\text{H}_5)_3.$
C	80.28 per cent.	80.49
H	5.19 „	4.87
O	14.53 „	14.63

This substance, therefore, is tribenzoylmethane. On heating, it melts at $224-225^\circ$, and sublimes at a higher temperature almost without decomposition; in this respect it seems to be an extremely stable compound. Tribenzoylmethane is almost insoluble in cold alcohol, more easily soluble in hot, and crystallises from this solvent on cooling in small, almost microscopic, colourless needles. The hot alcoholic solution gives an orange coloration on adding a drop of ferric chloride. It is fairly easily soluble in benzene and carbon bisulphide, and crystallises in small needles on evaporating the solution. In chloroform and ether, on the contrary, it is sparingly soluble, and in light petroleum almost insoluble. It dissolves readily in alcoholic potash, and on adding water forms a colourless solution from which acids precipitate the original compound unchanged. On warming with concentrated sulphuric acid, it is coloured yellow. Nitric acid appears to entirely decompose it. Experiments were next made in the hope of obtaining tetrabenzoylmethane by the further action of sodic ethylate and benzoyl chloride on tribenzoylmethane, thus:—



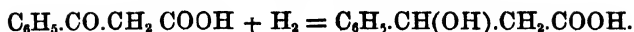
By this means, a small quantity of a colourless body was obtained which, after being extracted several times with boiling alcohol, melted between $260-270^\circ$, and gave the following results on analysis:—

	Found.	Theory. $\text{C}(\text{C}_6\text{H}_5\text{CO})_4.$	Theory. $\text{CH}(\text{C}_6\text{H}_5\text{CO})_3.$
C	81.43 per cent.	80.58	80.49
H	5.15 „	4.63	4.87
O	13.42 „	14.80	14.63

As will be seen from the above, the analysis of such a substance does not show whether it is a tetra- or tri-benzoylmethane. The only fact which seems to prove that tetrabenzoylmethane had been formed is that the product is far more sparingly soluble in alcoholic potash than tribenzoylmethane. I hope at some future time to be able to continue the study of these interesting compounds, and if possible to improve the methods of preparing them.

Reduction of Ethylic Benzoylacetate.

Benzoylacetic acid being a ketonic acid, it was thought that it would be interesting to study the action of nascent hydrogen on it, in order, if possible, to obtain β -phenyllactic acid according to the equation—



In this reaction, it is better to use ethylic benzoylacetate than the free acid; the following method gives good results.

Ethylic benzoylacetate is dissolved in dilute sodic hydroxide solution, care being taken to avoid any large excess of alkali, and then 5 per cent. sodium amalgam is added in small portions at a time. The amalgam liquefies at first without evolution of hydrogen, the liquid becoming so warm that it is necessary to cool it continually. After about ten hours, hydrogen begins to be evolved, and the reaction is finished. The product is then filtered from a small amount of a resinous body (which will be described later on), the filtrate acidulated with dilute sulphuric acid, and extracted several times with ether. On distilling off the ether, an almost colourless oily acid remains, which does not solidify even after long standing in a vacuum over sulphuric acid. In order to purify it, the whole is converted into the barium salt by agitation with baryta-water, the excess of baryta removed by carbonic anhydride, and the precipitated barium carbonate filtered off. The colourless solution of the barium salt of the acid so obtained, is acidified with hydrochloric acid, shaken several times with ether, and the ethereal solution dried over chloride of calcium. On distilling off the ether, a very thick colourless oil is left; and this, on standing for some time, solidifies almost completely, especially after scratching the sides of the vessel containing it with a sharp glass rod. It may be purified by crystallising it once or twice from benzene, when it is obtained in beautiful colourless nodules consisting of fine needles. It melts at 93—94°, and gave the following numbers on analysis:—

0.2005 gram substance gave 0.1100 gram H_2O and 0.4760 gram CO_2 .

	Found.	Theory. $\text{C}_6\text{H}_5\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{COOH}.$
C....	64.75 per cent.	65.06 per cent.
H....	6.09 ,,	6.03 ,,
O....	21.16 ,,	28.91 ,,

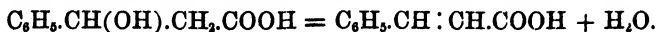
The substance was therefore β -phenyllactic acid, and was further identified by an analysis of the silver salt, which is easily obtained by precipitating a neutral solution of the ammonium salt with nitrate of silver, as a white curdy precipitate, somewhat soluble in water.

0.3360 gram substance gave 0.1330 gram Ag = 39.58 per cent.

Theory: $\text{C}_6\text{H}_5\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{COOAg} = 39.56$,,

On heating this silver salt, it decomposes into silver carbonic anhydride and cinnamene, almost without charring. The acid itself, when

carefully heated, splits up almost quantitatively into water and cinnamic acid, according to the equation—



This acid has all the properties of the β -phenyllactic acid prepared by Glaser (*Annalen*, 147, 86) by the action of sodium amalgam on phenylchlorolactic acid, $\text{C}_6\text{H}_5\cdot\text{CH}(\text{OH})\cdot\text{CHCl}\cdot\text{COOH}$, its formation from ethylic benzoylacetate being a proof that the hydroxyl group is really in the β -position. The same acid is also formed by boiling phenylbromopropionic acid, $\text{C}_6\text{H}_5\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{COOH}$, with water (Fittig and Binder, *Annalen*, 195, 138).

By the action of nascent hydrogen on ethylic benzoylacetate, there is always a certain amount of a resinous substance formed which separates out of the alkaline solution during the reduction, and can easily be freed from the sodic salt of the β -phenyllactic acid by filtration and washing with water. As in some cases a considerable amount of this compound was formed, it was thought that it might contain something definite, and was therefore carefully examined. The filter-papers were extracted with ether, and the ethereal solution filtered and evaporated; by this means a very thick dark-brown oil was left behind, which, after standing for several days, partly crystallised. The crystals were easily obtained colourless and free from oil, by repeated washings with small quantities of ether in which they are difficultly soluble. Last of all they were dissolved in a little hot alcohol, from which they crystallise on cooling in thick colourless prisms melting at 102° .

The analysis gave the following result:—

- I. 0.1665 gram substance gave 0.0768 gram H_2O and 0.4581 gram CO_2 .
 II. 0.2082 gram substance gave 0.0906 gram H_2O and 0.5720 gram CO_2 .

	Found.		Theory. ($\text{C}_6\text{H}_5\text{O}$) _n .
	I.	II.	
C	75.04	74.93 per cent.	75.00 per cent.
H	5.12	4.83 ,,	5.00 ,,
O	19.84	20.24 ,,	20.00 ,,

This substance therefore has the formula $(\text{C}_6\text{H}_5\text{O})_n$, most likely $\text{C}_{10}\text{H}_8\text{O}_2$.

When warmed with alcoholic potash, it yields an intense magenta-red solution; and on filtering and acidifying a colourless crystalline acid is precipitated. The alcoholic solution does not give any colour reaction with ferric chloride.

A small quantity of this body warmed with concentrated sulphuric acid dissolves, forming a pinkish solution with a slight greenish fluorescence. If, after standing for a short time, this solution be poured into water, a whitish amorphous substance separates; this forms an intense blue-green solution on the addition of an excess of sodic hydroxide. If the original substance, however, be more strongly heated with sulphuric acid, the pinkish colour first produced becomes browner, and at last of a deep olive-green. On pouring this olive-green solution into water, a bright yellowish liquid is produced, which, on the addition of sodic hydroxide, becomes of a beautiful purple. This reaction is extremely delicate, and is produced by mere traces of substance. This compound is isomeric with a substance which was obtained by the action of sodium on acetate of phenyl, a reaction which W. R. Hodgkinson and I studied some time ago (*Trans.*, 1880, 487). Curiously enough the latter also gives the same characteristic reaction when warmed with potash; the red colour is destroyed, however, on diluting with water, which is not the case with the body described above.

Action of Phosphorous Pentachloride on Ethylic Benzoylacetate.

Geuther (*Zeitschr. f. Chem.*, 1871, 237), who was the first to study the action of pentachloride of phosphorus on ethylic acetoacetate, found that when it was treated with an excess of the former it was resolved into the chlorides of two isomeric chlorcrotonic acids, namely, β -chlor- α -crotonic acid, $\text{CH}_3\text{CCl}:\text{CH}.\text{COOH}$, and the β -chloro- β -crotonic acid, $\text{CH}_2:\text{CCl}.\text{CH}_2.\text{COOH}$.

On decomposing these chlorides with water, and distilling with steam, the β -chloro- β -crotonic acid distils over first, and then the β -chloro- α -crotonic acid. As the methyl group of the ethylic acetoacetate must have taken part in the formation of β -chloro- β -crotonic acid, supposing the formula $\text{CH}_2:\text{CCl}.\text{CH}_2.\text{COOH}$ to be correct, it appeared interesting to repeat these experiments with ethylic benzoylacetate, in which the presence of the phenyl group would shut out the possibility of the formation of any acid analogous in constitution to β -chloro- β -crotonic acid.

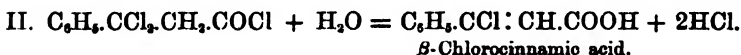
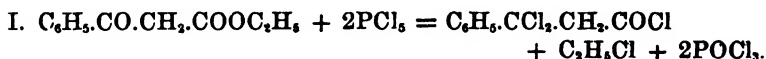
In order to test this, 10 grams of ethylic benzoylacetate was dissolved in 25 grams of oxychloride of phosphorus, and 25 grams of phosphorous pentachloride slowly added. As the reaction appeared to take place very slowly at ordinary temperatures, the mixture becoming only slightly warm, the whole was heated for about half an hour on a water-bath, when the pentachloride slowly disappeared, hydrogen chloride being given off. As soon as the reaction was over, the oxychloride of phosphorus was distilled off on a water-bath in a

vacuum, the latter portions carrying over a small quantity of a crystalline substance which sublimed into the condenser in yellow needles; these, however, were not further examined. The residue, consisting of a dark-brown oil, was poured into ice-water and allowed to remain for some time, in order that acid chlorides and any excess of pentachloride of phosphorus might be entirely decomposed. An excess of sodic carbonate was then added, and the whole gently warmed with animal charcoal on a water-bath for about fifteen minutes, and filtered. On acidifying the filtrate, which was nearly colourless, it deposited a crystalline acid; this was collected, well washed, and recrystallised twice from alcohol. It was thus obtained perfectly pure in beautiful glittering plates, which, on analysis, gave the following result:—

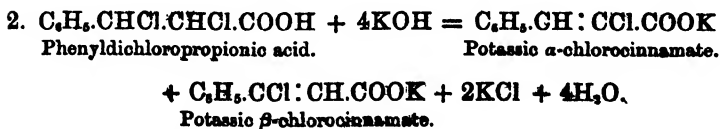
0.1798 gram substance gave 0.0665 gram H_2O and 0.3901 gram CO_2 .
 0.2424 " " 0.3080 $AgCl$.

	Found.	Theory. $C_8H_7O_2Cl$.
C	59.17 per cent.	59.18 per cent.
H	4.10 "	3.84 "
Cl	19.47 "	19.45 "
O	17.26 "	17.53 "

The compound was therefore chlorocinnamic acid, produced according to the equations—

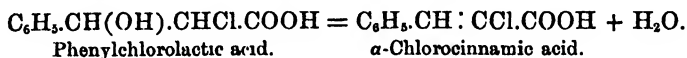


By this reaction, therefore, β -chlorocinnamic acid should be obtained. There are two monochlorocinnamic acids known, the α -monochlorocinnamic acid, $C_6H_5.CH:CCl.COOH$, and the β -monochlorocinnamic acid, $C_6H_5.CCl:CH.COOH$. These were obtained by Jutz (*Ber.*, 15, 788), in a way exactly similar to that employed by Glaser (*Annalen*, 143, 330), in the preparation of the monobromocinnamic acids, namely, by heating phenyldichloropropionic acid with potash:—

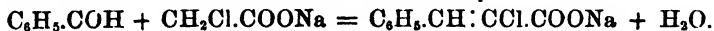


He separated these acids by means of the potash salts, the salt of

the α -acid being sparingly soluble in water, whereas the salt of the β -acid is easily soluble. The α -chlorocinnamic acid, crystallised from water, melts at 137—138°, crystallised from light petroleum at 142°. β -Chlorocinnamic acid melts at 114°. α -Chlorocinnamic acid is also formed by heating phenylchlorolactic acid with water at 120—200°:—



This is a proof that the chlorine is in the α -position, there being no doubt as to the constitution of phenylchlorolactic acid. A further proof of the constitution of α -chlorocinnamic acid is its formation by the action of acetic anhydride on a mixture of benzaldehyde with sodic monochloracetate, according to the equation—



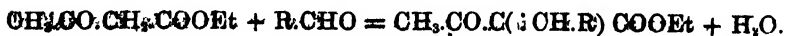
(Plöchl, *Ber.*, 15, 1945).

The chlorocinnamic acid obtained from ethyl benzoylacetate by the action of pentachloride of phosphorus in the way just described, melts at 142°, and possesses, strangely enough, all the properties of α -chlorocinnamic acid, with which it is no doubt identical, although, according to the equation given above, β -chlorocinnamic acid should be produced.

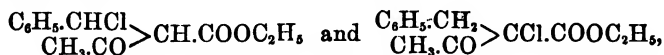
The formation of α -chlorocinnamic acid from ethyl benzoylacetate in this way is difficult to explain; one is forced to come to the conclusion that the β -acid is first formed, and afterwards, under the influence of such powerful reagents as pentachloride and oxychloride of phosphorus, that a molecular change takes place, whereby the β -acid is transformed into the α -acid. In the case of the monobromocinnamic acids, the β -acid can with the greatest ease be transformed into the α -acid by distillation, or by heating with hydriodic acid, the change being almost quantitative. Still stranger is the fact that the β -monobromocinnamic acid on etherification is converted quantitatively into the ethyl salt of α -monobromocinnamic acid. This mobility of the bromine-atom makes it appear possible that these compounds are merely physical isomerides, and not chemical isomerides in the true sense of the word.

Condensation of Ethyl Benzoylacetate with Benzaldehyde.

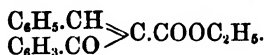
The hydrogen-atoms of the methylene group in ethyl acetoacetate are very easily substituted by condensation with aldehydes, according to the equation (Claisen, *Annalen*, 218, 170)—



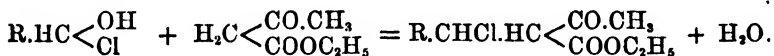
This condensation is best brought about by mixing the ethylic acetoacetate with the calculated amount of the aldehyde, and then after cooling in a freezing mixture, saturating the whole with hydrogen chloride. After standing for about two days, the reaction is complete, the resulting product, *e.g.*, in the case of the condensation of ethylic acetoacetate with benzaldehyde, consisting of a mixture of two isomeric ethylic acetylbenzylchloracetates—



which are easily separated by crystallisation from light petroleum. Both these compounds are decomposed by distillation, yielding hydrogen chloride and ethylic acetylbenzalacetate—



Claisen explains this condensation by supposing that the aldehyde is first converted by the hydrochloric acid into an unstable chlorhydrol, $\text{R}.\text{CH}(\text{OH})\text{Cl}$, which then acts on the ethylic acetoacetate in the following way:—



On substituting benzoylacetate for ethylic acetoacetate, it was found that condensation with aldehydes took place in precisely the same way. As it appeared interesting to prove the analogy between ethylic benzoylacetate and acetoacetate in this respect also, the condensation of the former with benzaldehyde was further studied.

10 grams of ethylic benzoylacetate were mixed with 5 grams of benzaldehyde, and the whole, after being cooled below 0° in a freezing mixture, was completely saturated with hydrogen chloride. The product soon became very thick and milky, from the formation of minute globules of water, which, after standing for 24 hours at the ordinary temperature, settled out in large drops on the side of the vessel.

The dark brown oily product was dissolved in ether, well washed, first with water and then with sodic carbonate solution, to remove the excess of hydrochloric acid, and finally dried over potassic carbonate. After filtering and distilling off the ether, a dark brownish very thick oil remained; this was distilled as rapidly as possible under diminished pressure (200 mm.), only a small residue being left. The distillate, which was nearly colourless, was distilled again, under the same pressure, the first portions, consisting of acetophenone and unchanged benzaldehyde, being rejected; afterwards a thick oil came over, which rapidly solidified on standing.

The latter was dissolved in hot methyl alcohol, from which on cooling it crystallised in beautiful colourless needles, easily obtained pure by recrystallisation.

The analysis of the crystals, dried at 70—80°, gave the following numbers:—

- I. 0.2243 gram of substance gave 0.1195 gram H_2O and 0.6321 gram CO_2 .
 II. 0.2022 gram of substance gave 0.1040 gram H_2O and 0.5665 gram CO_2 .

	Found.		Theory.
	I.	II.	$C_6H_5.CO.C \begin{matrix} \swarrow CH.C_6H_5 \\ \searrow COOC_2H_5 \end{matrix}$
C	76.86	76.83 per cent.	77.14 per cent.
H	5.91	5.74 „	5.72 „
O	17.23	17.43 „	17.14 „

The compound is therefore ethylic benzalbenzoylacetate. Ethylic benzalbenzoylacetate crystallises from methyl alcohol in long colourless glittering prisms, which melt at 98—99°. It is pretty easily soluble in hot methyl alcohol, sparingly so in cold. Like ethylic acetylbenzalacetate, it crystallises very readily. It separates from a mixture of benzene and light petroleum in flat plates, which polarise light splendidly. It crystallises best, however, from ether. If the ethereal solution is allowed to evaporate slowly, the sides and bottom of the vessel containing it become covered with large transparent glittering prisms, which do not lose their lustre on drying. Professor Haushofer, who kindly measured some of the crystals, gave me the following description of them:—

Crystalline system monoclinic:

$$a : b : c = 1.2730 : 1 : 0.7461. \quad \beta = 86^\circ 36'.$$

Pale yellow lustrous crystals, forming the combinations $\infty P\infty(a)$, $\infty P(p)$, $-P\infty(r)$, $P\infty(s)$, extended in the direction of the ortho-

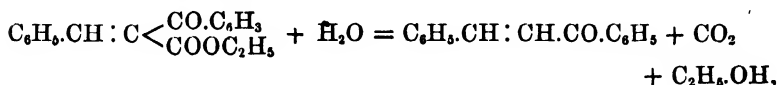


diagonal, often also tabular on the surface a . The surfaces of this zone are smooth, but as a rule indented, and the measurements are therefore somewhat irregular.

	Measured.	Calculated.
$p : p = 103^{\circ} 36'$		—
$r : p = 109$	37	—
$s : r = 119$	20	—
$r : a = 122$	57	$122^{\circ} 53'$
$p : a = 128$	30	128 12
$s : a = 117$	53	117 47
$s : p = 106$	40	106 45

Ethyl benzalbenzoylacetate dissolves in sulphuric acid, producing a yellow solution, which, however, becomes colourless again on standing or gently warming. The solution of this body in chloroform is only very slowly attacked by bromine.

Several saponification experiments were next made, in the hope of obtaining benzylideneacetophenone, according to the equation—



but without result. When ethyl benzalbenzoylacetate was heated with dilute hydrochloric acid in a sealed tube at 160° for seven hours, it was decomposed in part, producing a yellow oil. On opening the tube, large quantities of carbonic anhydride escaped, and on fractioning the product a considerable amount was obtained boiling below 210° , and consisting of a mixture of benzaldehyde and acetophenone. The thermometer was then removed, and the residue distilled in a vacuum, when a thick oil came over, which solidified on cooling. After crystallisation from methyl alcohol, it melted at 98° , and showed all the properties of ethyl benzalbenzoylacetate. Negative results were also obtained on boiling it with potash, only small quantities of benzoic acid being produced.

Claisen (*Annalen*, 218, 173) obtained similar results on trying to obtain ethylideneacetone and crotonic acid by saponifying ethyl acetyl ethylideneacetate, $\begin{smallmatrix} \text{CH}_3\cdot\text{CH} \\ \text{CH}_3\cdot\text{CO} \end{smallmatrix} \gg \text{C}\cdot\text{COOC}_2\text{H}_5$, with potash, and attributes this to the fact of the latter class of bodies being so easily decomposed into their components, and thus giving only aldehyde and the decomposition-products of ethyl acetate, respectively ethyl benzoylacetate on hydrolysis. Another method employed by Claisen to effect the condensation of aldehydes with ethyl acetate was by heating a mixture of the two bodies in a sealed tube with acetic anhydride. In order to see whether this also took place in the case of ethyl benzoylacetate, 10 grams of the latter, 5 grams of benzaldehyde, and an excess of acetic anhydride, were heated together in a sealed tube at 180 – 200° for six hours. On opening the

tube a large quantity of carbonic anhydride escaped. The product, which was a dark brown oil, was then directly fractioned. Below 100° , a small quantity of a limpid oil came over, which, after washing and refractioning, distilled almost entirely between 70° and 80° as a light oil, smelling strongly of ethylic acetate. After the excess of acetic anhydride and acetic acid had distilled over, the thermometer rose rapidly to 180° , and between that and 210° a considerable quantity of a mixture of benzaldehyde and acetophenone came over. The residue was then distilled under diminished pressure, when the latter portions, which were collected separately, partially solidified on cooling. The crystals were first roughly freed from oily matter, by spreading them out on a porous plate, and then purified by crystallisation, once from methyl alcohol and once from ether.

The analysis gave the following numbers:—

0.1863 gram substance gave 0.0976 gram H_2O and 0.5254 gram CO_2 .

	Found	Theory.
		$\begin{array}{c} C_6H_5 \cdot CO \\ C_6H_5 \cdot CH \end{array} > C \cdot COOC_2H_5$
C . . .	76.92 per cent.	77.14 per cent.
H . . .	5.82 „	5.72 „
O . . .	17.26 „	17.14 „

The crystals melted at 98° , and the body was therefore ethylic benzalbenzoylacetate. The yield by this method was not nearly so good as by the one previously described. It is possible that the temperature employed (180 — 200°) was too high, and that some of the product was again resolved into its components, the ethylic benzoylacetate being further decomposed into acetophenone and carbonic anhydride.

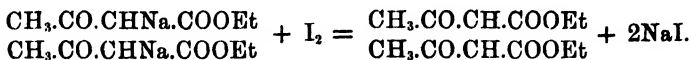
XXXIII.—On Benzoylactic Acid and some of its Derivatives. Part III.

By W. H. PERKIN (Jun.), Ph.D., Privatdocent at the University of Munich.

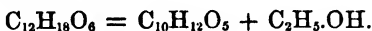
In the first two parts of this research, I described a number of simpler derivatives of ethylic benzoylacetate, showing it to be analogous to ethylic acetoacetate in almost every respect. In the third part, I wish to bring before the Society an account of some of the more complicated reactions into which this body enters, namely, the preparation and properties of ethylic dibenzoylsuccinate, ethylic monobenzoylsuccinate, and dehydrobenzoylactic acid.

Ethylic Dibenzoylsuccinate.

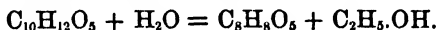
By the action of iodine on the sodium compound of ethylic acetoacetate, Harrow (Trans., 1878, 425) obtained ethylic diacetylsuccinate, according to the equation—



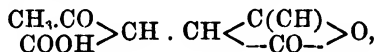
On boiling this compound with dilute sulphuric acid, it is partly hydrolysed, giving off one molecule of alcohol, and forming the ethylic salt of carbopyrotritaric acid, thus:—



If the saponifying action is continued further, this ethereal salt is split up into carbopyrotritaric acid and alcohol,—



This acid, which Harrow supposes to have the constitution—



is resolved, on further heating with dilute sulphuric acid, into pyrotritaric acid and carbonic anhydride, thus:—



On account of this latter reaction, Harrow assigns the following constitution to pyrotritaric acid:—



Considering the complicated nature of these reactions, it appeared to be interesting to repeat them with ethylic benzoylacetate, in order to determine whether similar compounds would be produced, corresponding with carbopyrotritaric and pyrotritaric acids.

It was necessary, in the first place, to prepare ethylic dibenzoylsuccinate, which can easily be effected by a method analogous to that employed by Harrow for preparing ethylic diacetylsuccinate, namely, by the action of iodine on ethylic benzoylsodacetate. 4·7 grams of the finely powdered sodium compound were mixed with dry ether, and 2·8 grams of iodine added in small quantities at a time, the whole being well shaken and cooled after each addition. At first the colour of the iodine disappears instantly, but towards the end of the reaction much more slowly, the mixture becoming slightly brownish.

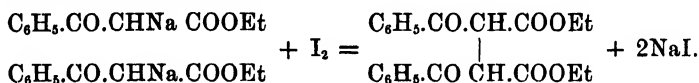
The ethereal solution is filtered from the precipitated sodic iodide, washed with water and a little sulphurous acid in order to remove any slight excess of iodine, and then dried over calcium chloride. On

distilling off the ether, a brownish mass remains, which becomes almost entirely solid when exposed for about 24 hours over sulphuric acid in a vacuum. These crystals are spread out on a porous plate, in order to remove as much of the mother-liquor as possible, washed on a filter, with small quantities of ether, until an almost colourless mass remains behind, and purified by two crystallisations from alcohol.

0.1630 gram substance gave 0.0890 gram H_2O and 0.4113 CO_2 .

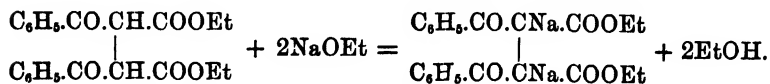
	Found.	Theory, $C_{12}H_{12}O_6$
C.....	68.82 per cent.	69.11 per cent.
H.....	6.06 „	5.76 „
O.....	25.12 „	25.13 „

The compound is therefore ethylic dibenzoylsuccinate, formed according to the equation—



Ethylic dibenzoylsuccinate melts at 128—130°, and when heated in a test-tube it is decomposed, a carbonaceous residue being left. It is sparingly soluble in cold alcohol, but easily in hot, being deposited from this solution on cooling in short thick prisms; it may be obtained perfectly colourless by repeated recrystallisation. It is easily soluble in ether and benzene, crystallising in small needles on evaporation.

The behaviour of ethylic dibenzoylsuccinate with concentrated sulphuric acid is very characteristic. The finely powdered substance dissolves in the acid, forming an almost colourless solution, and on adding water is reprecipitated apparently unchanged. When the solution is heated, it becomes first reddish and then olive-green, but if the heating is continued the colour changes to a bluish-red. If this solution when cold is poured into a little water, a brownish liquid is obtained, with a strong blue fluorescence; an excess of water destroys the coloration altogether. As ethylic benzoylsuccinate contains two CH groups which are each joined on both sides to carbonyl groups, it appeared very probable that it might yield a disodium compound on treatment with sodium ethoxide, according to the equation—



This was in reality found to be the case, the compound being best formed in the following way: 0.3 gram of sodium is dissolved in the smallest possible quantity of alcohol, and while still warm an excess of pure dry ether is added, the whole being thoroughly mixed, by

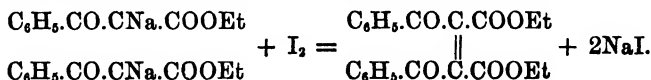
means of a glass rod, until the liquid becomes clear, or only slightly turbid. An ethereal solution of 2.5 grams of ethylic dibenzoylsuccinate is then added, and the whole allowed to stand for some time. The sodium compound slowly separates out as a slightly yellowish mass, and as soon as the precipitation is finished it is collected by means of a vacuum pump, and well washed, first, with a mixture of alcohol and ether, and lastly, with ether, in which the compound is almost insoluble. The disodium compound was thus obtained as an almost colourless mass, which, after standing for some hours over sulphuric acid in a vacuum, gave the following numbers on analysis:—

0.4434 gram substance gave 0.1575 Na_2SO_4 .

	Found.	Theory.
Na	11.49 per cent.	10.80 per cent.

When perfectly dry, this compound is fairly stable, but if it contains a little alcohol it quickly takes up moisture from the air, and is decomposed. It is fairly soluble in hot alcohol, sparingly in the cold. On adding a drop of ferric chloride to the alcoholic solution, a dirty red coloration is formed. Cupric acetate precipitates the copper salt as a light-green amorphous mass. The sodium compound is easily decomposed by dilute acids, the original substance being apparently regenerated.

If this compound is treated with an ethereal solution of iodine, sodium iodide is instantly precipitated, and on filtering and evaporating the ethereal solution a thick brownish oil is obtained, which is probably ethylic dibenzoylfumarate produced according to the equation—



The oil, unfortunately, would not crystallise, and therefore a good analysis could not be obtained. The solution in chloroform, however, decolorised bromine instantly, without evolution of hydrobromic acid, showing that it is an unsaturated compound.

Decomposition Products of Ethylic Dibenzoylsuccinate.

On mixing ethylic dibenzoylsuccinate with alcoholic potash, it dissolves, producing an intensely yellow solution. If after allowing it to remain for some time, or gently warming, the product be acidulated with dilute sulphuric acid, a yellow amorphous acid is precipitated; unfortunately, however, this could not be obtained in a crystalline state, as it is extremely soluble in all solvents except water. In order to purify it as far as possible, it was dissolved in ammonia, and

fractionally precipitated with dilute acid; this treatment having been repeated several times, the product was finally converted into the silver salt, and analysed with the following result:—

0·3047 gram substance gave 0·1171 gram Ag.

Found.	Theory, $\text{Ag}_3\text{C}_{18}\text{H}_{12}\text{O}_6$.
Ag 38·43 per cent.	40·00 per cent.

Although these numbers do not agree very closely with theory, it is yet probable that the substance is in reality impure dibenzoylsuccinic acid. On adding ferric chloride to the solution of the acid in alcohol, or that of the ammonium salt, a peculiar dark-green precipitate is formed, closely resembling that obtained with sulphuric acid.

The acid dissolves in concentrated sulphuric acid, producing a yellowish solution which becomes of a beautiful crimson on warming. The acid gives acetophenone when distilled with soda-lime. From the above experiments, it appeared unlikely that better results would be obtained by saponifying with other alkalis, such as baryta-water, and it was thought probable that, as in the case of ethylic diacetylsuccinate, dilute acids might be employed with greater advantage. The following method of hydrolysis was finally adopted.

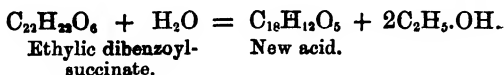
Pure ethylic dibenzoylsuccinate was boiled with an excess of dilute sulphuric acid (1 : 2) for about six hours in a flask connected with a reflux condenser, at the end of which a test-tube containing baryta-water was fixed. The mass became more and more darkly coloured, but very little carbonic anhydride was given off. When cold, the product was collected, washed with water, well shaken with a warm solution of sodic carbonate, and filtered. The residual tarry mass was then washed with water, again boiled with dilute sulphuric acid for six hours, and the extraction with sodic carbonate repeated as before. The greater part dissolved, leaving a thick black residue, from which mere traces of an organic acid were obtained on repeating the treatment with sulphuric acid.

The different alkaline solutions were mixed and acidified with dilute sulphuric acid. This produced a precipitate which, after being recrystallised several times from dilute acetic acid (70 per cent.), was obtained pure in the form of small colourless needles which gave the following numbers on analysis:—

I. 0·1862 gram substance gave 0·0664 H_2O and 0·4752 CO_2 .	
II. 0·2032 " " " 0·0745 H_2O " 0·5249 CO_2 .	
III. 0·1627 " " " 0·0592 H_2O " 0·4167 CO_2 .	

	Found.			Theory. $C_{18}H_{12}O_5$.
	I.	II.	III.	
C . . .	69·60	70·42	69·85 per cent.	70·13 per cent.
H . . .	3·96	4·07	4·04 „	3·89 „
O . . .	26·44	25·51	26·11 „	25·97 „

The formula of this acid is therefore $C_{18}H_{12}O_5$, and it is formed from ethylic dibenzoylsuccinate by the removal of 2 mols. of alcohol, thus :—



its formation corresponding precisely with that of carbopyrotritaric acid from ethylic diacetylsuccinate :—



This new acid melts at 236—238°. It is easily soluble in ether, alcohol, benzene, light petroleum, and glacial acetic acid, less so in a 70 per cent. solution of the latter solvent, from which it crystallises in small needles. The alcoholic solution gives an orange coloration with ferric chloride.

This acid, $C_{18}H_{12}O_5$, dissolves in concentrated sulphuric acid, forming a colourless solution, which however acquires a beautiful violet colour when warmed. Heated by itself in a test-tube, it first melts and then sublimes, water being given off at the same time. The sublimate is crystalline, but apparently insoluble in ammonia, and is perhaps the anhydride of the acid. The acid $C_{18}H_{12}O_5$ is easily decomposed on distilling it with soda-lime, acetophenone being formed. Its alcoholic solution does not appear to react with phenylhydrazine or hydroxylamine. It is, however, a strong acid, dissolving easily in ammonia, sodic hydroxide, or sodic carbonate solutions. The ammonium salt was prepared by dissolving the acid in ammonia and then allowing the solution to stand over sulphuric acid in a vacuum until the excess of alkali had evaporated. On adding silver nitrate to this solution, a white precipitate of the silver salt was formed; this, when dried over sulphuric acid in a vacuum, gave the following numbers on analysis :—

0·4817 gram substance gave 0·1939 gram silver.

	Found.	Theory.	
		$C_{18}H_{10}O_4Ag_2$.	$C_{18}H_{12}O_5Ag_2$.
Ag . . .	40·25 per cent.	41·29 per cent.	40·00 per cent.

This result not being satisfactory, a complete analysis of the silver salt was made with the following result :—

0.2683 gram substance gave 0.400 CO₂, 0.0562 H₂O and 0.1087 Ag.

		Theory.	
		C ₁₈ H ₁₀ O ₅ Ag ₂ .	C ₁₈ H ₁₂ O ₆ Ag ₂ .
C	40.66 per cent.	41.44	40.00 per cent.
H	2.32 "	1.91	2.22 "
Ag ...	40.52 "	41.29	40.00 "
O	16.50 "	15.35	17.77 "

This silver salt is very stable, being only slowly discoloured on standing in the air by daylight. The solution of the ammonium salt gives the following reactions:—Barium chloride precipitates the *barium salt* as a white amorphous mass, insoluble in water, but slightly soluble in alcohol. The *calcium salt* is thrown down by calcium chloride as a heavy, white, amorphous powder insoluble in water. Dried at 100° and analysed, it gave the following result:—

0.2625 gram substance gave 0.0949 gram CaSO₄.

		Theory.	
		C ₁₈ H ₁₀ O ₅ Ca.	C ₁₈ H ₁₁ O ₆ Ca.
Ca....	10.63 per cent.	11.56 per cent.	10.99 per cent.

The *copper salt* is precipitated on the addition of cupric sulphate as a light green, almost colourless mass, which is very sparingly soluble in water. It dissolves in ammonia and sodic hydroxide solution with a blue colour.

On boiling these solutions, the salt is decomposed, copper oxide being precipitated.

Ferric chloride produces a reddish-brown precipitate, very much resembling that produced in solutions of benzoic acid or its salts.

Ferrous sulphate gives no precipitate.

On adding a solution of acetate of lead, the *lead salt* is thrown down as a heavy white mass, almost insoluble in water.

If a solution of zinc sulphate be added to the ammonia salt, the whole remains clear for some time, but after standing the *zinc salt* slowly separates out as a white powder which is somewhat soluble in hot water.

The *nickel salt* is formed on adding a solution of sulphate of nickel as a light-green precipitate, which is soluble in ammonia, producing a beautiful blue solution.

Action of Acetic Anhydride on the Acid C₁₈H₁₂O₆.

In order to obtain some clue as to the constitution of this acid, several experiments were tried with different reagents, mostly without

result. On heating it with acetic anhydride, however, it was found that the acid easily gave up the elements of water, being converted into an indifferent body according to the equation—



In order to examine this new compound, the pure acid, $\text{C}_{18}\text{H}_{12}\text{O}_5$, was heated with an excess of acetic anhydride for about an hour in a flask connected with a reflux condenser. On cooling, the solution which had become slightly yellowish was diluted with water and allowed to remain until the excess of acetic anhydride had dissolved. During this operation, a beautifully crystalline substance separated, which was collected, well washed with water, recrystallised once from acetic acid, and analysed, with the following result:—

0.1961 gram substance gave 0.0670 gram H_2O and 0.5329 gram CO_2 .

	Found.	Calculated. $\text{C}_{18}\text{H}_{10}\text{O}_4$.
C. . . .	74.11 per cent.	74.48 per cent.
H . . .	3.79 ,,	3.45 ,,
O. . . .	22.10 ,,	22.07 ,,

It melts at 254—255° with slight decomposition. If heated carefully in a test-tube, the greater part sublimes, but considerable decomposition takes place, and a black residue is left. The sublimate is crystalline, and probably identical with that obtained by treating the acid $\text{C}_{18}\text{H}_{12}\text{O}_5$ in the same way. The compound $\text{C}_{18}\text{H}_{10}\text{O}_4$ is sparingly soluble in hot alcohol, yielding a solution with a most beautiful violet fluorescence very much like that exhibited by anthracene. It is nearly insoluble in cold alcohol. The solution in hot alcohol gives an orange coloration with ferric chloride. The substance crystallises beautifully from its solution in hot glacial acetic acid, which on cooling deposits it in glittering plates. It is easily soluble in hot benzene, and on adding light petroleum is precipitated in a beautifully crystalline condition. It is easily soluble in chloroform, but only sparingly in ether or bisulphide of carbon. It dissolves in concentrated sulphuric acid, yielding a yellowish-green solution which changes to a violet colour on warming.

The compound $\text{C}_{18}\text{H}_{10}\text{O}_4$ is neutral, being almost insoluble in ammonia and potash solution, and apparently quite insoluble in sodic carbonate solution.

Action of Potash on the Compound $\text{C}_{18}\text{H}_{10}\text{O}_4$.

If this substance is warmed with fairly concentrated alcoholic potash, it dissolves without becoming discoloured or any apparent decomposi-

tion taking place. In order to further examine this reaction, the liquid was heated for ten minutes on a water-bath, and then diluted with water, when the whole dissolved, forming a slightly yellowish solution. On adding dilute sulphuric acid, a solid acid was precipitated, which was collected, well washed with water, dissolved in alcohol, and filtered; in this way a small quantity of unchanged $C_{18}H_{10}O_4$ was easily removed. On evaporation, the filtrate deposited a solid crystalline acid, which after recrystallising from dilute acetic acid was analysed with the following result:—

0.1865 gram substance gave 0.0668 gram H_2O and 0.4758 gram CO_2 .

	Found.	Calculated. $C_{18}H_{12}O_5$.
C. . .	69.58 per cent.	70.13 per cent.
H . .	3.98 „	3.89 „
O . .	26.44 „	25.97 „

This substance was, therefore, the original acid, $C_{18}H_{12}O_5$, formed from the compound $C_{18}H_{10}O_4$ by the addition of water according to the equation—



It melted at $230-235^\circ$, and had all the properties of the acid obtained by the action of dilute sulphuric acid on ethylic dibenzoylsuccinate.

Constitution of the Acid $C_{18}H_{12}O_5$.

Harrow by the action of dilute sulphuric acid on ethylic diacetylsuccinate (Trans., 1878, 428) obtained carbopyrotritaric acid, $C_8H_8O_5$, which from his analyses of its salts would seem to be a monobasic acid. When boiled with potash, however, it is converted into the potash salt of a bibasic acid, $C_8H_6O_6$, which gives salts of the formula $C_8H_5O_6M_2$.

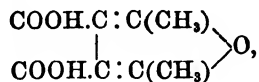
The acid $C_{18}H_{12}O_5$ is, however, either bibasic or else very easily converted into a bibasic acid, as it gives directly salts containing two atoms of the metal; unfortunately from the analyses it is not clear whether these have the formula $C_{18}H_{10}O_5M_2$ or $C_{18}H_{12}O_6M_2$. It is, however, possible that these acids, $C_{18}H_{12}O_5$ and $C_8H_8O_5$, are in reality anhydro-acids, the former acid when dissolved in ammonia or alkalis being converted into salts of an unstable acid, $C_{18}H_{14}O_6$.

Since the publication of an abstract of this research (Ber., 17, 59), the carbopyrotritaric acid has been more thoroughly examined by Knorr (Ber., 17, 2863), who considers it to be a bibasic acid, forming salts of the formula $C_8H_6O_6Ag_2$. On account of the formation of ethylic carbopyrotritarate by the action of concentrated sulphuric

acid on ethylic diacetylsuccinate in the cold, according to the equation—

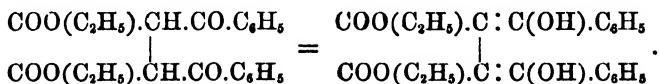


Knorr comes to the conclusion that carbopyrotritaric acid must have the following constitution :—

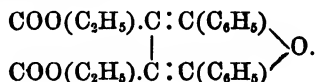


it being, in fact, dimethylfurfuranedicarboxylic acid. Since the publication of Knorr's research, I have tried the action of concentrated sulphuric acid on ethylic dibenzoylsuccinate, and found that it behaves in exactly the same way as the diacetylsuccinate, although, unfortunately, having very little material at my command, I have not been able to analyse the intermediate product corresponding with the ethylic carbopyrotritarate.

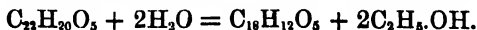
Ethylic dibenzoylsuccinate dissolves easily in concentrated sulphuric acid, the mixture becoming slightly warm and brownish coloured. If water be added to it after standing for 15 hours, an oil is precipitated which soon becomes solid. This was extracted with ether, and on allowing the solution to evaporate, a beautiful substance was obtained crystallising in long thick prisms melting at 85°. This is undoubtedly the diethyl salt of the acid $C_{18}H_{12}O_5$, as on saponification with potash it gives the acid in a perfectly pure state, melting at 236—237°. In order to explain the formation of this acid, $C_{18}H_{12}O_5$, it is necessary in the first place to suppose the formula of ethylic dibenzoylsuccinate transformed into an isomeric unstable modification, thus :—



On treating this with sulphuric acid, water is eliminated, the diethyl salt of diphenylfurfuranedicarboxylic acid being formed, which therefore has the following constitution :—



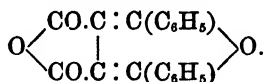
On saponification, this salt gives the acid $C_{18}H_{12}O_5$, thus :—



The acid $C_{18}H_{12}O_5$ is, therefore, without doubt, in reality diphenylfurfuranedicarboxylic acid.

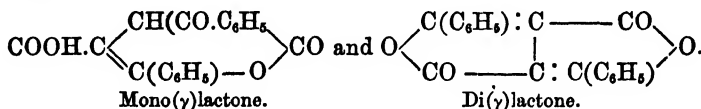
The compound $C_{18}H_{10}O_4$, produced by the action of acetic anhydride

on diphenylfurfuranedicarboxylic acid, is probably the anhydride of the acid, it being reconverted into the same by the action of alkalis. Its constitution would, therefore, be represented by the formula—



A further examination of these compounds is, however, necessary before these points can be settled.

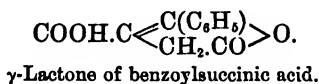
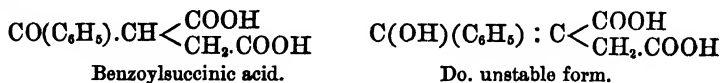
In the paper published in the *Berichte (loc. cit.)*, the splitting off of the water was supposed to take place between the carboxyl-groups COOH.C : C(OH)Ph and the hydroxyl-groups in the compound COOH.C : C(OH)Ph , the acid $\text{C}_{18}\text{H}_{12}\text{O}_5$ being a mono(γ)lactone and the compound $\text{C}_{18}\text{H}_{10}\text{O}_4$ a di(γ)lactone of dibenzoylsuccinic acid, and therefore having the formulæ—



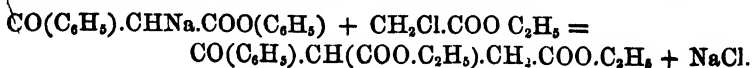
From Knorr's experiments, however, it would seem that his explanation of the formation of these bodies is the most probable, and that they are furfurane-derivatives and not lactones.

Ethylic Monobenzoylsuccinate.

The examination of this substance was undertaken in the hope of throwing further light on the constitution of the compounds mentioned in the preceding section. If the acid $\text{C}_{18}\text{H}_{12}\text{O}_5$ is the γ -lactone of dibenzoylsuccinic acid, it was thought probable that the corresponding γ -lactone of monobenzoylsuccinic acid might be obtained by the action of dilute sulphuric acid on ethylic monobenzoylsuccinate, thus:—



Ethylic benzoylsuccinate is easily obtained by treating the sodium compound of ethylic benzoylacetate with ethylic monochloracetate.



It was prepared as follows :—2·5 grams of sodium were dissolved in 30 grams of absolute alcohol, and then after well cooling, 20 grams of ethylic benzoylacetate and 12 grams of ethylic monochloracetate slowly added. The reaction takes place very slowly in the cold, but rapidly on a water-bath, the mixture after heating for two hours becoming perfectly neutral. In order to isolate the product, the alcohol was distilled off, and the residue then dissolved in water; by this means a heavy oil separated out which was extracted with ether. After drying over calcium chloride and distilling off the ether, a thick brownish oil was obtained, which unfortunately could not be made to crystallise.

On trying to distil this in a vacuum, it was found that only a small quantity went over undecomposed, the principal part frothing up and charring, a quantity of gas being at the same time given off. It is, however, comparatively easy to distil small quantities of about 5 grams, if the distillation is rapidly conducted. The distillates from several such operations were united and fractioned once or twice, when an oil was obtained boiling at 260—265° (160 mm.); this gave the following numbers on analysis, agreeing with the formula of ethylic benzoylsuccinate:—

0·1557 gram substance gave 0·0905 gram OH_2 and 0·3695 CO_2 .

	Found.	Theory.
C	64·72 per cent.	64·75 per cent.
H	6·46 „	6·47 „
O	28·82 „	28·78 „

As thus obtained, it is a thick, almost colourless, oil, of an agreeable aromatic smell, somewhat resembling that of ethylic benzoate. It boils at 260—265° (at 160 mm.). The pure compound is very stable, and may be distilled at the ordinary pressure, apparently without much decomposition. It is insoluble in water, but mixes with alcohol, ether, and the usual solvents. As on examination it was found that the crude product consisted of almost pure ethylic benzoylsuccinate, and as the distillation entailed great loss of valuable material, the crude compound was used in the following reactions and decompositions, after the excess of ethylic benzoylacetate had been removed by shaking the ethereal solution several times with dilute potash solution.

On the addition of a drop of ferric chloride to the solution of ethylic benzoylsuccinate in alcohol a beautiful claret colour is produced. If heated for some hours on an oil-bath at about 250°, ethylic benzoylsuccinate is decomposed, lower boiling aromatic oils being formed, which, however, could not be further examined, on account of the smallness of the quantity obtained. It dissolves in concentrated

sulphuric acid, producing a yellow solution, which becomes intensely red when heated.

It is decomposed by heating with alcoholic potash, a violet solution being produced, which on acidifying deposits a solid acid melting at 118—120°, probably benzoic or benzoylpropionic acid.

Like ethylic dibenzoylsuccinate, ethylic monobenzoylsuccinate gives a sodium compound when treated with sodium ethoxide.

This compound is easily prepared in the following way:—0.3 gram of sodium is dissolved in a small quantity of absolute alcohol, and then pure dry ether added until the whole has nearly dissolved. A solution of 3.5 grams of ethylic benzoylsuccinate in ether is then poured in, and the whole allowed to remain for some time. The mixture becomes violet coloured, and a gelatinous precipitate slowly separates, which is collected, and washed, first with a mixture of ether and alcohol, and lastly with pure ether. Dried over sulphuric acid in a vacuum, it gave the following numbers:—

0.2601 gram substance gave 0.0680 gram Na_2SO_4 .

	Found.	Theory.
		$\text{C}_{16}\text{H}_{17}\text{NaO}_5$.
Na	8.47 per cent.	7.67 per cent.

It is a hard, almost colourless, apparently amorphous mass, which is moderately soluble in alcohol. If cupric acetate is added to this solution, the copper derivative is precipitated as a pale green amorphous mass, almost insoluble in water, but soluble in sodic hydroxide, producing a blue solution. Nitrate of silver and acetate of lead give white precipitates with the alcoholic solution of the sodium derivative. The sodium compound is very stable, much more so than the disodium derivative of ethylic dibenzoylsuccinate. The powdered substance is easily decomposed by treatment with acids, a yellowish oil being precipitated, probably regenerated ethylic monobenzoylsuccinate.

Decomposition Products of Ethylic Benzoylsuccinate.

Hydrolysis with Baryta-water.—Before examining the products of the hydrolysis with dilute sulphuric acid, it appeared to be interesting to study the action of alkalis, and for this purpose, experiments were made with potash, but as this did not appear to give promising results, baryta-water was afterwards substituted for it, the method employed being the following:—

Ethylic benzoylsuccinate was heated in a flask with an excess of a concentrated solution of barium hydroxide, by which means hydrolysis rapidly set in, the reaction being complete in about an hour. During the operation the oil disappeared, without the liquid becoming

much discoloured, and a heavy sandy precipitate of a brownish colour slowly separated. This was collected, washed with water, and decomposed with hydrochloric acid, when traces of carbonic anhydride were given off. After extracting several times with ether, a dark brown oil was obtained, which began to deposit crystals after some time. These were separated from the oily mother-liquor by extracting with chloroform, and thus obtained in a perfectly colourless state, melting at 180° , and having all the properties of succinic acid. In order to confirm this, the silver salt was prepared and analysed with the following result:—

0.2024 gram substance gave 0.1306 gram silver.

	Found.	Theory. $C_4H_4O_4Ag_2$.
Ag	64.52 per cent.	65.07 per cent.

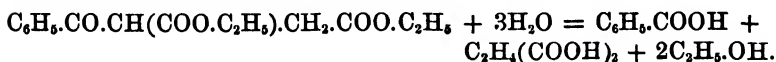
On acidifying with hydrochloric acid the filtrate from the precipitated baric succinate, it gave a quantity of a beautifully crystalline acid, which was collected, well washed, and recrystallised once or twice from water. It was thus obtained in silky needles melting at $118-120^{\circ}$, and was therefore either benzoic or benzoylpropionic acid. A silver salt was made and analysed with the following result:—

0.1976 gram substance gave 0.0936 gram silver.

	Found.	Theory. C_6H_5COOAg .	Theory. $C_6H_5COCH_2CH_2COOAg$.
Ag	47.37 per cent.	47.16 per cent.	37.82 per cent.

The acid was evidently benzoic acid.

Ethylc benzoylsuccinate is therefore decomposed by boiling with concentrated baryta water into benzoic and succinic acids, thus:—



In this respect it differs somewhat from ethylc acetylsuccinate, which on hydrolysis with dilute baryta-water, is split up into acetylpropionic acid and carbonic anhydride, only a small quantity of acetic acid and succinic acid being formed (Conrad, *Annalen*, 118, 218).

Ethylc benzoylsuccinate, if treated with dilute baryta-water, might also be split up in this way into benzoylpropionic acid and carbonic anhydride.

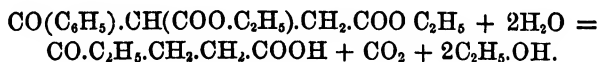
Hydrolysis with Dilute Sulphuric Acid.—Ethylc benzoylsuccinate was heated with a large excess of dilute sulphuric acid (1 : 2) in a flask connected with a reflux condenser, at the end of which a test-tube containing baryta-water was attached. The oil became

more and more darkly coloured, and large quantities of carbonic anhydride were given off, until at the end of about 15 hours most of the ethereal salt had dissolved, a small quantity of a tarry substance being left. On cooling, the liquid became filled with glittering crystals, which were collected, well washed with water, roughly separated from oily mother-liquor by spreading out on a porous plate, and then recrystallised once or twice from water, animal charcoal being used to decolorise the liquid. In this way, the body was obtained in glittering plates melting at 117° , and closely resembling benzoic acid. The analysis, however, showed the body to be benzoylpropionic acid.

0.2230 gram substance gave 0.1132 gram OH_2 and 0.5487 gram CO_2 .

	Found.	Theory. $\text{C}_{10}\text{H}_{10}\text{O}_3$.
C	67.12 per cent.	67.41 per cent.
H	5.64 „	5.62 „
O	27.24 „	26.97 „

Ethyl benzoylsuccinate splits up, therefore, on boiling with dilute sulphuric acid into benzoylpropionic acid and carbonic anhydride according to the equation—



Benzoylpropionic acid has already been obtained (1) by the action of aluminic chloride on a mixture of succinic anhydride and benzene (Burcker, *Bull. Soc. Chim.*, **35**, 17), and by the reduction of benzoylacrylic acid (Pechmann, *Ber.*, **14**, 889). The acid obtained from ethyl benzoylsuccinate agrees with that produced by the above two reactions in every respect.

By modifying the conditions in the hydrolysis of *ethyl benzoylsuccinate* with dilute sulphuric acid, the same results were always obtained, no lactone ever being formed. The reason for this is that the C_2H_5 group of the $\text{COO}.\text{C}_2\text{H}_5$, which is joined to the $\text{C}_6\text{H}_5.\text{CO}.\text{CH}$, in benzoylsuccinic ether, is always split off first, forming the unstable acid $\text{C}_6\text{H}_5.\text{CO}.\text{CH}(\text{COOH}).\text{CH}_2.\text{COO}.\text{C}_2\text{H}_5$, which then naturally loses carbonic anhydride, and is converted into ethyl benzoylpropionate, this being then further hydrolysed by the action of the sulphuric acid. Analogous results were obtained by Conrad (*Ber.*, **11**, 2177) by the action of dilute sulphuric acid on ethyl acetylsuccinate, acetylpropionic acid, ethyl acetylpropionate and carbonic anhydride being the products of the reaction.

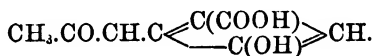
Dehydrobenzoylacetic Acid.

Among the many reactions in which ethylic acetoacetate takes part, there are few more interesting than the condensation which this body undergoes on prolonged boiling; by this treatment, 2 molecules appear to combine, with elimination of 2 molecules of alcohol and formation of dehydracetic acid, according to the equation—



This acid, the constitution of which, in spite of many experiments, still remains to be explained, was first obtained by Geuther (*Zeit. f. Chem.*, 1866, 8) by passing carbonic anhydride over the heated sodium derivative of ethylic acetoacetate. During the reaction, a quantity of ethylic acetoacetate distils over, and the sodium salt of dehydracetic acid remains in the retort. On dissolving the latter in water and acidifying with dilute sulphuric acid, the acid is set free, and by repeated recrystallisation from water can easily be obtained pure in colourless leafy crystals melting at 109°.

Geuther proved this compound to be a monobasic acid, forming salts of the formula $\text{C}_8\text{H}_7\text{O}_4\text{M}$. At a more recent date, Oppenheim and Precht (*Ber.*, 9, 324, 1100) undertook the further investigation of the acid, and succeeded in preparing a number of derivatives, which they carefully examined, and from the results proposed the following as the most probable constitutional formula:—



This formula presupposes that, in the formation of this acid from 2 molecules of the acetoacetate, the methyl-group of one molecule takes part in the reaction, whereas the methyl-group of the second molecule remains intact. In order to test the accuracy of this formula, it appeared interesting to determine whether it would be possible under the same conditions to obtain a similar body from ethylic benzoylacetate, in which case the two phenyl-groups would be excluded from taking part in the condensation.

The constitution of an aromatic compound of this kind would probably be much easier to determine, and if it were found that its derivatives behaved in a way exactly analogous to those of dehydracetic acid itself, it would be legitimate to suppose that the methyl-groups of the two molecules of ethylic acetoacetate which went to form dehydracetic acid did not take part in the reaction.

In the first experiments on ethylic benzoylacetate, it was noticed that on distilling this body rapidly a great part went over as a colourless oil, a considerable quantity of a black tarry mass being left

behind, partly soluble in carbonate of soda solution on continued agitation. On filtering and acidifying the alkaline solution, an acid was deposited in the form of brownish flakes; this by repeated recrystallisation from alcohol was obtained pure in the form of long yellow needles. As it was thought possible that this might be the desired acid, numerous experiments were made in order to find some means of obtaining it in larger quantity. The following process was found to give the best results:—

Ethyl benzoylacetate was first heated to boiling in portions of 10—15 grams in test-tubes or small retorts for 7—8 minutes, during which operation the mass gradually became darker, whilst a quantity of lower boiling oil was given off; this was collected for further examination. On cooling, the residue generally solidified to a brownish cake of crystals. The distillate from a number of such operations was first examined. On fractioning, the principal portion passed over between 70° and 110°, then the thermometer rose rapidly to 180°, between which temperature and 210° a considerable quantity distilled; a small residue was left, which appeared to consist in great part of unchanged ethyl benzoylacetate. The fraction 70—110°, which had a strongly acid reaction, was mixed with dry carbonate of potash, and after remaining for some time, distilled on a water-bath. On further fractioning, the distillate went over almost to the last drop between 78 and 80°, and possessed all the properties of common alcohol. The residual potash salt was then acidulated with dilute sulphuric acid and distilled in steam; a strongly acid liquid passed over, which showed all the reactions of acetic acid. The fraction 70—110° was therefore a mixture of alcohol and acetic acid.

On refractioning the fraction 180—210°, nearly the whole distilled over between 190—200°, and was from its odour easily recognised as acetophenone. This was confirmed by warming it with a solution of orthonitrobenzaldehyde in dilute sodic hydroxide, when a copious precipitate of indigo was slowly formed.

The solid residue from these experiments was then boiled for a considerable time with alcohol and animal charcoal, and filtered, the new acid crystallising out in long yellow needles on cooling. On distilling off the alcohol from the mother-liquor of these crystals, it deposited a quantity of a dark brown oil; on heating this again in the way described above, it gave a new quantity of acid. This treatment was repeated until the residual oil on further heating no longer solidified on cooling, but remained behind as a blackish tarry mass, which, however, still contained considerable quantities of the acid. In order to extract this, the whole was dissolved in a little alcohol, enough potash added to neutralise the acid, the product diluted with water, and several times extracted with ether. On acidifying the solution of the

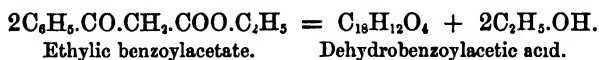
potash salt, the acid was deposited in a crude state, and was treated with alcohol and animal charcoal as described above.

The different crops of crystals were then mixed together, crystallised several times from alcohol, and thus obtained pure. The analysis gave the following numbers :—

- I. 0.1879 gram substance gave 0.0715 gram H_2O and 0.5082 gram CO_2 .
 II. 0.2577 gram substance gave 0.0958 gram H_2O and 0.6978 gram CO_2 .
 III. 0.1941 gram substance gave 0.0746 gram H_2O and 0.5241 gram CO_2 .
 IV. 0.1974 gram substance gave 0.0740 gram H_2O and 0.5319 gram CO_2 .

	Found.					Theory.
	I.	II.	III.	IV.		$\text{C}_{18}\text{H}_{12}\text{O}_4$.
C	73.76	73.85	73.64	73.49	per cent.	73.97 per cent.
H	4.22	4.13	4.27	4.16	„	4.11 „
O	22.02	22.02	22.09	22.35	„	21.92 „

This substance, for which I propose the name dehydrobenzoylacetic acid, has therefore the formula $\text{C}_{18}\text{H}_{12}\text{O}_4$, and is formed from 2 molecules of ethylic benzoylacetate in a way exactly analogous to the formation of dehydracetic acid from ethylic acetoacetate, according to the equation—



This acid crystallises from its solution in hot alcohol in long yellow needles which melt at $171\text{--}172^\circ$. It is moderately soluble in hot alcohol, but only sparingly in the cold. On the addition of a drop of ferric chloride to the hot alcoholic solution, it gives a deep orange-red coloration. Dehydrobenzoylacetic acid dissolves easily in benzene, chloroform, bisulphide of carbon, and ether, but sparingly so in light petroleum. On evaporating these solutions, the acid crystallises out beautifully in long yellow needles. The solution in bisulphide of carbon does not decolorise bromine in the cold, and only very slowly on boiling, hydrogen bromide being given off. This behaviour is exactly analogous to that of dehydracetic acid, which, when treated with bromine, forms a substitution-product, $\text{C}_6\text{H}_7\text{O}_4\text{Br}$, and not an additive product, as might be expected, considering the small percentage of hydrogen which the acid contains.

Dehydrobenzoylacetic acid dissolves in concentrated sulphuric acid with an olive-green colour; on warming, a beautiful violet solution is

obtained, which, when examined with the spectroscope, gives exactly the same absorption-spectrum as indigo.

The acid is not acted on, even by prolonged heating with acetic anhydride, being precipitated unchanged on adding water, a proof that the dehydrobenzoylacetic acid contains no hydroxyl-groups.

The acid chars when submitted to dry distillation, a quantity of gas being given off; but if heated with soda-lime, acetophenone is formed.

Dehydrobenzoylacetic acid readily combines with phenylhydrazine, forming an intensely yellow compound, which is difficult to purify, and has not as yet been analysed. The pure acid dissolves easily in ammonia, soda, and sodic carbonate, forming yellow solutions.

The ammonium salt was obtained in the usual way, by allowing the solution of the acid in ammonia to stand over sulphuric acid in a vacuum until the excess of alkali had been removed. The following salts were prepared by precipitation:—Silver nitrate causes the precipitation of the silver salt as a yellowish-white flocculent mass, which is very stable and only slowly acted on by light. It was collected, well washed with water, dried at 100°, and analysed with the following result:—

0.2949 gram substance gave 0.0818 gram H_2O , 0.5874 gram CO_2 , and 0.0786 gram silver.

	Found.	Theory. $C_{18}H_{11}O_4Ag$.
C	54.32 per cent.	54.19 per cent.
H	3.08 "	2.75 "
Ag	26.65 "	27.00 "
O	15.95 "	16.06 "

Dehydrobenzoylacetic acid is therefore a monobasic acid. The *ferric salt* is thrown down as a beautiful scarlet precipitate on adding ferric chloride to a solution of the ammonium salt. Ferrous sulphate, on the contrary, gives a blackish-violet precipitate, the behaviour with these two reagents being a very characteristic reaction for the acid. The *copper salt* is obtained, on adding cupric sulphate, as a light greenish precipitate, soluble in ammonia. The *lead*, *calcium*, *barium*, *zinc*, and *tin salts* are heavy white precipitates, almost insoluble in water. *Nickel sulphate* gives, with a solution of the ammonium salt, a light green almost colourless precipitate, soluble in ammonia. All these salts are extremely stable.

If ethylic benzoylacetate is boiled as described above for about eight minutes, the only condensation-product formed in any quantity is dehydrobenzoylacetic acid. If, however, the boiling is continued

for a longer time, the reaction becomes more and more complicated, higher condensation-products being formed.

In order to study these, and, if possible, to determine their constitution, the ethylic benzoylacetate was heated in small retorts in quantities of from 10 to 15 grams for about half an hour, during which time alcohol and acetophenone were given off continuously and fairly regularly. The black tarry residue, which became semi-solid on cooling, was found to contain at least two condensation-products besides dehydrobenzoylacetic acid; these were separated as follows:— In order to remove the dehydrobenzoylacetic acid the mass was first treated with a moderately concentrated solution of ammonia and allowed to stand, the whole being well stirred from time to time. After filtering off the aqueous solution of the ammonium salt, the residue was well washed with water, and then several times extracted with hot alcohol; this removed all the colouring matter, and left a yellowish amorphous mass, which will be described further on.

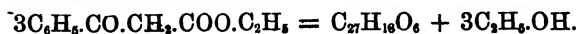
The dark brown alcoholic solution was digested for a long time with animal charcoal, filtered, and the bulk of the alcohol distilled off. On cooling, a beautifully crystalline body separated, which was purified by repeated recrystallisation.

The analysis gave numbers agreeing with the formula $(C_{27}H_{18}O_6)_n$.

- I. 0.2343 gram substance gave 0.0941 gram H_2O and 0.6374 gram CO_2 .
 II. 0.1746 gram substance gave 0.0709 gram H_2O and 0.4722 gram CO_2 .

	Found.		Theory. $(C_{27}H_{18}O_6)_n$.
	I.	II.	
C. . . .	74.19	73.76 per cent.	73.97 per cent.
H . . .	4.41	4.51 "	4.11 "
O . . .	21.40	21.73 "	21.92 "

This compound probably has the formula $C_{27}H_{18}O_6$; being formed from 3 mols. of ethylic benzoylacetate by the elimination of 3 mols. of alcohol, according to the equation—



This substance melts at 273—275°. It is sparingly soluble in cold alcohol, more easily in hot, and crystallises on cooling in beautiful silky plates, which strongly resemble anthracene, and give a beautiful play of colours with polarised light. It is almost insoluble in benzene, light petroleum, and acetone. In ether and carbon bisulphide, it is somewhat soluble, and on evaporation crystallises in glittering plates. The solution in carbon bisulphide is only very slowly acted on by bromine, hydrogen bromide being given off. On adding an

etheral solution of sodium ethoxide to the solution of the substance in warm ether, a voluminous precipitate of a sodium compound is thrown down; this is decomposed by treatment with acids with regeneration of the original compound.

This substance, however, is not a true acid. It dissolves easily in dilute alcoholic soda or sodium ethoxide, but is entirely reprecipitated on passing carbonic anhydride, so that in this case a sodium compound, corresponding with that of ethylic benzoylacetate is formed, and not the sodium salt of an acid. If the solution in alcoholic potash is allowed to remain for some time, the compound is slowly but completely decomposed. On diluting the product with water, and acidifying with dilute sulphuric acid, an acid is precipitated which has all the properties of benzoylactic acid. It melts at $80-85^{\circ}$, gives the characteristic violet coloration with ferric chloride, and is decomposed into carbonic anhydride and acetophenone on heating. This acid appears to be produced almost quantitatively by the action of potash on the substance $C_{27}H_{18}O_6$.

If it is boiled with alcoholic potash, benzoic acid, acetophenone, and other bodies are formed. Heated in a test-tube, the compound $C_{27}H_{18}O_6$ sublimes partly unchanged, but most of it is decomposed, with separation of oily bodies, probably acetophenone. When distilled with zinc-dust, a light boiling body is given off, which burns with a strongly luminous flame, and appears to be benzene. It is not decomposed by boiling with dilute sulphuric acid. It dissolves in concentrated sulphuric acid with a faint yellowish colour, which is not perceptibly changed on warming. It is easily attacked by hot concentrated nitric acid, and on adding water to the product a yellowish mass is precipitated, which crystallises beautifully from alcohol, and is probably a nitro-derivative. On warming the compound $C_{27}H_{18}O_6$ with phenylhydrazine, it yields an intensely yellow body, which, however, was not further examined.

The yellow amorphous compound, mentioned above (p. 281) as remaining when the compound $C_{27}H_{18}O_6$ was dissolved by treating the crude product with alcohol, was then further examined.

This substance melts above 300° . It is insoluble in most of the usual solvents, and can therefore be easily separated from impurities by repeated extraction with them. It is thus obtained as a light yellow amorphous mass, which gave the following numbers on analysis:—

I. 0.1243 gram substance gave 0.0460 gram H_2O and 0.3380 gram CO_2 .

II. 0.1556 gram substance gave 0.0586 gram H_2O and 0.4239 gram CO_2 .

	Found.		Theory.
	I.	II.	(C ₃₆ H ₂₄ O ₈) _n .
C	74.16 per cent.	74.29 per cent.	73.97 per cent.
H	4.11 "	4.18 "	4.11 "
O	21.73 "	21.53 "	21.92 "

The compound appears to be homogeneous, the above analyses having been made with two distinct preparations. It is possible that it may have the formula C₃₆H₂₄O₈, being a condensation-product of 4 mols. of ethylic benzoylacetate, 4C₆H₅.CO.CH₂.COO.C₂H₅ = C₃₆H₂₄O₈ + 4C₂H₅.OH. It is an acid, and dissolves easily in sodium ethoxide, being reprecipitated by dilute sulphuric acid, but not by carbonic anhydride. It is also partially soluble in ammonia. On boiling it with sodium ethoxide, a deep red solution is formed; this, when acidified, deposits a small quantity of an acid, the alcoholic solution of which gives a violet coloration with ferric chloride. The following is an extremely characteristic reaction of this substance. If the merest trace of it is mixed with concentrated sulphuric acid, it dissolves to a yellowish solution; and on warming this the colour changes slowly to a reddish-brown and then to a reddish-violet. If this solution be further heated, a most intense bluish-violet coloration is produced, which becomes purple on strongly heating. The bluish-violet coloration is most beautiful, and strongly resembles methylene-blue. The colour disappears on diluting with water.

Owing to the difficulty of obtaining any quantity of these last two condensation-products, I have not examined them further, but confined my attention to the dehydrobenzoylacetate.

Ethylic Dehydrobenzoylacetate.

In order to prepare this ethereal salt, silver dehydrobenzoylacetate was digested on a water-bath for two hours with excess of ethyl iodide and a little dry ether; in this way the salt was completely decomposed. After collecting and extracting the precipitated iodide of silver several times with ether, and evaporating the ethereal solution, a semi-solid mass was obtained, which was first spread on a porous plate to free the crystals from oily matter, and then several times recrystallised from benzene. When analysed, it gave the following results:—

0.1843 gram of substance gave 0.0858 gram H₂O and 0.5050 gram CO₂.

	Found.	Theory.
		C ₁₇ H ₁₁ O ₂ .COOC ₂ H ₅ .
C	74.73 per cent.	75.00 per cent.
H	5.17 "	5.20 "
O	20.00 "	20.00 "

This compound is, therefore, ethylic dehydrobenzoylacetate. It crystallises from benzene in almost colourless glittering needles which melt at 159° , and show a beautiful play of colours when examined with the polariscope. If carefully heated, it appears to distil almost without decomposition.

It is moderately soluble in alcohol, acetone, benzene, and bisulphide of carbon, more sparingly in ether and light petroleum. The solution in alcohol gives a reddish-brown coloration on the addition of a drop of ferric chloride. Warmed with alcoholic potash, it is easily saponified, dehydrobenzoylactic acid being generated.

Its alcoholic solution when mixed with phenylhydrazine yields an intensely yellow compound which, however, has not yet been obtained pure enough for analysis; its formation is, however, a proof that the dehydrobenzoylactic acid contains at least one carbonyl-group.

If an ethereal solution of ethylic dehydrobenzoylacetate is treated with an ethereal solution of sodic ethylate, an intensely yellow sodium compound is precipitated; but, unfortunately, ethylic dehydrobenzoylacetate is so sparingly soluble in ether, that it was found impossible to obtain the compound in quantity sufficient for analysis.

In the course of some experiments on dehydracetic acid, the results of which I hope to have the honour of laying before the Society at some future time, it was found that the methyl salt of this acid possesses the property of forming a sodium compound of the formula $C_6H_5O_4CH_3Na$, in which one hydrogen of the methyl compound is directly replaced by sodium.

It is extremely probable, therefore, that the sodium compound of ethylic dehydrobenzoylacetate is similarly constituted.

Action of Potassic Hydroxide on Dehydrobenzoylactic Acid.

Dehydracetic acid is, as is well known, easily split up by heating with alkalis, into acetone, acetic acid, and carbonic anhydride, according to the equation—



It appeared likely, therefore, that by treating dehydrobenzoylactic acid in the same way, similar decomposition-products would be produced; thus affording evidence that this acid and dehydracetic acid were analogous compounds.

In order to test this, the action of potash on dehydrobenzoylactic acid was carefully studied in the following way:—

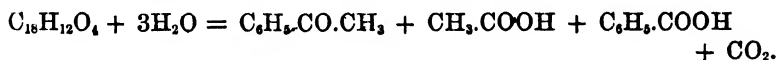
The pure acid was first dissolved in dilute alcoholic potash, and after an excess of a concentrated solution of the latter had been added, the whole was heated to boiling on a water-bath for several hours.

During the reaction the mass became gradually darker; when finished, the smell of acetophenone was easily recognisable.

In order to isolate the products, the alcohol was first slowly distilled off, water was then added, and the whole distilled in a current of steam. The distillate, which smelt strongly of acetophenone, contained small particles of oil, which were separated from the watery liquid by shaking with ether. On evaporating the ether, a colourless oil remained, which, on fractioning, went over entirely between 195—200°, and was undoubtedly acetophenone. This was confirmed by shaking it with a solution of orthonitrobenzaldehyde in dilute soda; in a short time an indigo-blue precipitate separated in considerable quantity.

The alkaline solution which was freed from the acetophenone in the way above described was acidified with dilute sulphuric acid, and again distilled, when an acid liquid passed over which smelt distinctly of acetic acid; the quantity, however, was so small that an analysis could not be performed. The residue in the retort was then several times extracted with ether; and on evaporating the solution, a dark-brown semi-solid acid was obtained. This was first separated from oily matter by spreading it out on a porous plate, and then recrystallised from water. In this way, it was obtained in colourless needles melting at 118—120°, and possessing all the properties of benzoic acid, with which it was undoubtedly identical.

Dehydrobenzoylacetic acid is therefore decomposed on heating with alcoholic potash into acetophenone, acetic acid, benzoic acid, and carbonic anhydride, according to the equation—



The reaction is perfectly analogous to the formation of 2 mols. of acetic acid and one of acetone by the action of potash on dehydracetic acid.

In the course of these experiments, it was noticed that when the boiling with potash was continued for a short time only, the benzoic acid obtained was always mixed with a certain quantity of another acid, the alcoholic solution of which gave a violet coloration with ferric chloride, strongly resembling that produced by benzoylacetic acid. In order, if possible, to obtain this acid in larger quantity, the action of potash on dehydrobenzoylacetic acid was tried in the cold, and it was found that it was completely decomposed if mixed with a concentrated solution of alcoholic potash, and allowed to remain for 12 hours. The mass became dark reddish-brown, and in a short time a considerable quantity of a potash salt crystallised out in glittering plates. On adding water, the whole dissolved, forming a reddish-

brown solution, which smelt only very faintly of acetophenone. In order to isolate the products of the reaction, the alkaline liquid was well cooled, acidified with dilute sulphuric acid, and once or twice extracted with ether. On allowing the ethereal solution to evaporate, a quantity of a dark-brownish acid was left, which was purified from oily matter by spreading it out on a porous plate, and thus obtained as a slightly yellowish, hard, crystalline mass. This was dissolved in dilute ammonia, well shaken with pure animal charcoal, and filtered. In this way an almost colourless solution of the ammonium salt was obtained, which was acidified with dilute sulphuric acid and extracted with ether. The ethereal solution, on evaporation, deposited a faintly yellowish-coloured crystalline acid; this after drying over sulphuric acid in a vacuum, gave the following numbers on analysis:—

0.1796 gram of substance gave 0.0841 gram H_2O and 0.432 gram CO_2 .

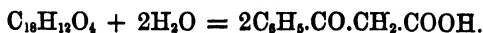
	Found.	Theory $C_9H_9O_3$
C	65.62 per cent.	65.85 per cent.
H	5.23 „	4.88 „
O	29.15 „	29.27 „

This acid has, therefore, the same constitution as benzoylactic acid, and is undoubtedly identical with it. It melted at $83-85^\circ$ (after recrystallising from benzene at $98-100^\circ$), and exhibited all the properties of benzoylactic acid. The solution in alcohol gives an intense violet coloration with ferric chloride, and the free acid, when distilled, is split up into acetophenone and carbonic anhydride. In order to be certain that the acid obtained from the dehydrobenzoylactic acid really had the constitution $C_9H_9O_3$, it was converted into the silver salt, and analysed with the following result:—

0.1463 gram substance gave 0.0592 gram silver.

	Found.	Theory. $C_9H_7COCH_2COOAg$.
Ag	40.36 per cent.	39.84 per cent.

There is, therefore, no doubt that dehydrobenzoylactic acid, when treated with alcoholic potash in the cold, is converted into benzoyl-acetic acid according to the equation—



This reaction is exactly the reverse of its formation from 2 mols. of ethylic benzoylacetate.

In order to determine whether this decomposition really did take

place according to the above reaction, some quantitative experiments were made, and the amount of benzoylactic acid produced weighed. 3 grams of pure dehydrobenzoylactic acid were mixed with a concentrated solution of alcoholic potash, and allowed to stand at the ordinary temperature until a very faint smell of acetophenone was perceptible. The product was then treated as described above. After evaporating the ethereal extract of the acid formed in a weighed dish, 3.15 grams of crude product were obtained (calculated for the above equation 3.3 grams). After spreading it out on a porous plate, and thus removing a trace of oily matter, the almost colourless acid left weighed nearly 3 grams. It was then treated with ammonia and animal charcoal, and gave 2.8 grams of nearly pure benzoylactic acid.

In order to be sure that this acid was benzoylactic acid, it was heated in a retort until the whole was decomposed, and the resulting oil dissolved in ether and shaken with a dilute solution of sodic hydroxide. On acidifying the alkaline solution and extracting with ether, a very small quantity of benzoic acid was obtained. The neutral oil formed by the decomposition showed the boiling point of 195° , and was undoubtedly acetophenone. It is probable therefore that on boiling dehydrobenzylactic acid with potash benzoylactic acid is first formed, which is then further decomposed into benzoic acid, acetic acid, acetophenone, and carbonic anhydride.

Reduction of Dehydrobenzoylactic Acid.

Dehydrobenzoylactic acid, $C_{18}H_{12}O_4$, besides the carboxyl-group, contains 2 atoms of hydrogen, one of which at least must be present in the ketone form, CO, from the fact that the acid combines with phenylhydrazine. This phenylhydrazine compound could be obtained crystalline only with difficulty, and then in such small quantity that a complete analysis could not be made, but only a nitrogen determination, which seemed to show that the body had the formula $C_{18}H_{12}O_3.N_2H.C_6H_5$, 1 mol. of the acid combining with 1 mol. of phenylhydrazine. In order to obtain some idea as to the condition of the fourth oxygen-atom in the molecule $C_{18}H_{12}O_4$, it was next treated with reducing agents under different conditions, the best results being obtained with sodium amalgam in the following way.

Dehydrobenzoylactic acid was dissolved in dilute sodic hydroxide and an excess of liquid sodium amalgam slowly added, the whole being well cooled during the operation, and the product allowed to stand for 24 hours in order to ensure complete reduction.

At first no evolution of hydrogen was perceptible, but towards the end of the reaction a quantity of gas was given off and a small

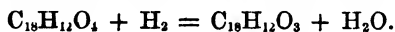
amount of a resinous body formed, which was filtered off from the alkaline solution, but was too small for further examination. On acidifying the filtrate with dilute sulphuric acid, it deposited an almost colourless, amorphous acid, which was collected, well washed with water, and spread out on a porous plate to free it from traces of oily matter. This crude product was dissolved in a little boiling benzene and then light petroleum boiling at 70—80° added until a slight turbidity was produced. On standing, this solution deposited a quantity of a new acid in colourless plates, which were obtained pure by recrystallisation from benzene and light petroleum.

The analysis gave the following numbers:—

- I. 0.1665 gram substance gave 0.0761 gram H_2O and 0.4750 gram CO_2 .
 II. 0.1485 gram substance gave 0.0669 gram H_2O and 0.4247 gram CO_2 .
 III. 0.1782 gram substance gave 0.0723 gram H_2O and 0.5097 gram CO_2 .

	Found.				Theory.
	I.	II.	III.		$C_{18}H_{12}O_3$.
C	77.81	77.99	78.09	per cent.	78.26 per cent.
H	5.07	5.00	4.51	„	4.35 „
O	17.12	17.01	17.40	„	17.39 „

This acid, therefore, has the formula $C_{18}H_{12}O_3$, and is produced from dehydrobenzoylacetic acid by the addition of 2 atoms of hydrogen and the elimination of the elements of water according to the equation—

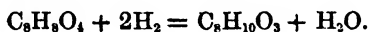


The yield of this acid is very small, and it appears to be formed only under certain conditions, the principal product of the reaction being the acid $C_{18}H_{14}O_4$, which will be described later on. In this reduction, by far the greater part of the dehydrobenzoylacetic acid is entirely decomposed, a quantity of oily and resinous product being formed, which render the purification of the acids very difficult. It is curious that a considerable quantity of benzaldehyde always appears to be formed during the reduction. The acid $C_{18}H_{12}O_3$ melts at 112°. It is easily soluble in alcohol, benzene, ether, chloroform, and bisulphide of carbon, almost insoluble in light petroleum. It is difficult to obtain it well crystallised, a mixture of benzene and light petroleum being the best solvents to crystallise it from. The bisulphide of carbon solution does not decolorise bromine.

The acid dissolves in concentrated sulphuric acid with an intense orange coloration which, on warming, first disappears and then turns to a greenish-brown.

Apparently it is a very stable body, and is not affected by potassium permanganate in the cold, and only slowly on warming. Heated by itself in a test-tube, it is decomposed into carbonic anhydride and high boiling oils, a considerable quantity of carbonaceous matter being left behind. No acetophenone is formed when it is distilled with soda-lime.

The acid dissolves in soda and ammonia slowly in the cold, more rapidly on heating. The sodium salt is best prepared by dissolving the acid in a little alcohol, neutralising with soda, and allowing the solution to evaporate over sulphuric acid in a vacuum. Thus obtained it is an almost colourless syrup easily soluble in water; the solution, exposed for a long time over sulphuric acid in a vacuum, slowly deposits crystals. The quantity of this acid, $C_{18}H_{12}O_3$, which I obtained was unfortunately insufficient to allow of the further examination and analysis of its salts. The products of the reduction of dehydracetic acid were first examined by Oppenheim and Precht (*Ber.*, 9, 1101) who, by treating this body with zinc and hydrochloric acid, obtained an acid melting at 187° ; this, however, they did not further examine, only stating that it was not a simple reduction-product, but that it appeared to contain less oxygen than the dehydracetic acid. Schibbye (*Inaugural Dissertation*, Würzburg, 1882), who during some experiments on dehydracetic acid, repeated this reaction, and analysed the acid and its barium salt, gave to the former the formula $C_8H_{10}O_3$, it being formed from dehydracetic acid according to the equation—



If the reaction takes place in this way, it is possible that the acid $C_{18}H_{12}O_3$, described above, is constituted similarly to the acid $C_8H_{10}O_3$, in which case the constitution of the former would have to be changed to $C_{18}H_{14}O_3$. I am at present engaged in some experiments to decide this point.

In order to isolate any other products of the reaction of dehydrobenzoylacetic acid, the mother-liquors from the acid $C_{18}H_{12}O_3$, were next evaporated to dryness, the semi-solid residue dissolved in a little alcohol, and light petroleum boiling at $70-80^\circ$ added until the liquid became slightly turbid. On allowing the solution to evaporate at the ordinary temperature, a new acid crystallised out in small needles, which were collected, washed with alcohol and light petroleum, and dried at 110° . The analysis gave the following results:—

- I. 0.1568 gram substance gave 0.0731 gram H_2O and 0.4239 gram CO_2 .
- II. 0.1614 gram substance gave 0.0758 gram H_2O and 0.4364 gram CO_2 .

III. 0.1511 gram substance gave 0.0705 gram H_2O and 0.4064 gram CO_2 .

	Found.				Theory. $C_{18}H_{14}O_4$.
	I.	II.	III.		
C	73.73	73.74	73.36	per cent.	73.47 per cent.
H	5.18	5.22	5.18	,,	4.76 ,,
O	21.09	21.04	21.46	,,	21.76 ,,

The acid, therefore, has the formula $C_{18}H_{14}O_4$, and is formed from dehydrobenzoylactic acid by the addition of 2 atoms of hydrogen, according to the equation—



It crystallises from a mixture of alcohol and light petroleum in small yellow needles which melt at $145-150^\circ$ with decomposition and evolution of carbonic anhydride. It is easily soluble in most of the usual solvents, but only sparingly in light petroleum and cold bisulphide of carbon. From its hot solution in the latter, it is deposited on cooling in nodules, seldom in well-formed crystals. The solution in bisulphide of carbon does not decolorise bromine at ordinary temperatures, but on warming hydrogen bromide is given off, and a brominated acid formed which crystallises out in small needles on cooling.

The acid $C_{18}H_{14}O_4$ is moderately soluble in dilute alkalis, especially on warming, and is reprecipitated on the addition of an acid. It dissolves in concentrated sulphuric acid, forming a yellow solution, which changes to brownish-red on warming. When heated in a test-tube, it melts and gives off carbonic anhydride, a low-boiling oil distilling over with an odour like benzene; if the heating be continued the greater part chars, a small quantity of a heavy oil being formed which becomes solid on cooling, and appears to be benzoic acid. On distilling the acid with soda-lime, a small amount of an oil of low boiling point is formed, but no acetophenone.

Action of Acetic Anhydride on the Acid $C_{18}H_{14}O_4$.

From the formula of this acid, it would seem to be the intermediate product in the formation of the acid $C_{18}H_{12}O_4$ by the reduction of dehydrobenzoylactic acid, thus:—



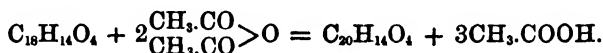
It appeared probable, therefore, that by treating it with some dehydrating agent, such as acetic anhydride, the acid $C_{18}H_{12}O_4$ would be produced. In order to test this, 2 grams of the acid $C_{18}H_{14}O_4$ were heated with an excess of acetic anhydride in a flask connected with

a reflux condenser for about one hour. Water was then added, and the precipitated product after washing with water was crystallised from 80 per cent. acetic acid. The analysis gave the following result:—

- I. 0.1910 gram substance gave 0.0817 gram H_2O and 0.5292 gram CO_2 .
 II. 0.2124 gram substance gave 0.0908 gram H_2O and 0.5871 gram CO_2 .

	Found.		Theory.
	I.	II.	$C_{20}H_{14}O_4$.
C	75.57	75.39 per cent.	75.47 per cent.
H	4.75	4.75 "	4.40 "
O	19.68	19.86 "	20.13 "

This compound appears therefore to have the formula $C_{20}H_{14}O_4$, and it would seem as if the acetic anhydride had not only acted as a dehydrating agent, but that an acetate had also been formed, according to the equation—



It is, however, impossible to come to any definite conclusion from this result, as the amount of material at my disposal was so small that I was unable to try this reaction again, and confirm the constitution of the compound $C_{20}H_{14}O_4$ by further analyses. It crystallises from acetic acid in yellow needles which melt at $145-150^\circ$. Heated in a test-tube, it first melts, and then gives off carbonic anhydride and acetic anhydride. From the ease with which it gives up its acetic anhydride, it is possible that it is nothing more than a mixed anhydride of the acid $C_{18}H_{12}O_3$ and acetic acid. It is easily soluble in hot alcohol, less so in cold. It dissolves easily in benzene and chloroform, but only sparingly in ether and bisulphide of carbon: in light petroleum it is almost insoluble. It is precipitated in small needles from its solution in benzene on adding light petroleum, and can be purified in this manner. It crystallises, however, best from dilute acetic acid (80 per cent.).

The alcoholic solution gives an intense scarlet coloration with ferric chloride. The compound is moderately soluble in ammonia, sodium hydroxide, and carbonate, especially on warming. It dissolves in concentrated sulphuric acid, forming an orange solution, which changes to brown on heating. This coloration does not disappear on diluting with water.

Heated with alcoholic potash, it is easily saponified, acetic acid and another acid being formed.

Action of Phosphorous Pentachloride on Dehydrobenzoylacetic Acid.

In order, if possible, to obtain some further clue as to the constitution of dehydrobenzoylacetic acid, it was next treated with phosphorous pentachloride. By this means, not only the carboxyl-group, but also any carbonyl- or hydroxyl-groups would be acted on, and be replaced by chlorine, whereas any oxygen present in the indifferent or oxide form would remain intact, and could be easily recognised.

If dehydrobenzoylacetic acid is mixed with phosphorous pentachloride, a very energetic reaction sets in, the whole becoming very hot and most of the acid being charred, so that it was found impossible to extract any crystalline compound from the product. It was necessary therefore to moderate the violence of the reaction by diluting with oxychloride of phosphorus and cooling, the experiment being carried out in the following way:—

5 grams of dehydrobenzoylacetic acid were mixed with 30 grams of phosphorous oxychloride, and then 10 grams of phosphorous pentachloride were slowly added, the whole being kept thoroughly cooled with ice-water. The acid slowly dissolved in the mixture, forming a yellowish-brown solution, and on standing, a quantity of yellow crystals were deposited, which, however, at a later stage of the reaction, disappeared again almost entirely. After remaining for 12 hours, the product was poured into ice-water, when a yellowish semi-solid mass was precipitated; this was collected, well washed with water, and dried over sulphuric acid in a vacuum. In about 48 hours, the mass, which had become hard and brittle, was powdered and extracted with small quantities of hot alcohol, in which it was sparingly soluble, and filtered. The filtrate on cooling deposited a yellowish crystalline substance, which by one or two recrystallisations from methyl alcohol, was obtained pure in colourless plates melting at 227—229°.

The amount of this compound obtained by the above reaction, was however, so small, that no analysis could be made. It appeared to contain only traces of chlorine. It is coloured yellow on being warmed with potash.

The residue left after extracting the above described substance with alcohol, was dissolved in boiling methyl alcohol, from which it was deposited on cooling in beautiful brownish-coloured glittering plates. On repeated recrystallisation from the same solvent it was easily obtained pure. For the analysis it was dried at 120° and then gave the following results:—

I. 0.2114 gram substance gave 0.0692 gram H_2O and 0.5370 gram CO_2 .

- II. 0.2226 gram substance gave 0.0758 gram H_2O and 0.5668 gram CO_2 .
 III. 0.1394 gram substance gave 0.0665 gram $AgCl$.
 IV. 0.2363 " " 0.1110 "
 V. 0.2415 " " 0.1128 "

	Found.					Theory.
	I.	II.	III.	IV.	V.	$C_{18}H_{11}O_3Cl$.
C	69.28	69.44	—	—	—	69.56 per cent.
H	3.63	3.78	—	—	—	3.55 "
Cl ...	—	—	11.80	11.63	11.58	11.43 "

The compound, therefore, has the formula $C_{18}H_{11}O_3Cl$. When crystallised from methyl alcohol, it forms brownish-coloured plates melting at $150-151^\circ$.

It is sparingly soluble in ether, alcohol, benzene, and light petroleum, more easily in hot methyl alcohol and acetic acid. The hot alcoholic solution gives a reddish-brown coloration with ferric chloride. It dissolves with difficulty in sodium hydroxide, ammonia, and sodium carbonate, forming yellow solutions, which, when acidified, deposit a colourless amorphous acid. On boiling with alcoholic potash for a short time, however, it is easily decomposed, and on evaporating the alcohol and adding water, a dark-brownish solution of a potassium salt is obtained; this, when acidified, deposits an oily acid, which was extracted with ether. On allowing the ethereal solution to evaporate, a thick oily acid was obtained, and on standing a small quantity of a crystalline body was deposited; this, however, could not be obtained pure enough for analysis. The alcoholic solution of this acid gives an intense violet coloration with ferric chloride, very similar to that produced by benzoylacetic acid. As the formation of this latter acid appeared possible, the crude product of the above reaction was distilled, and a few drops of a brownish oil obtained, which smelt decidedly of acetophenone. The quantity was too small, however, to determine the boiling point, and I was therefore unfortunately unable to decide definitely whether benzoylacetic acid had been formed or not. It appears, however, to be extremely probable. On simply warming the compound $C_{18}H_{11}O_3Cl$ with alcoholic potash, it dissolves completely, and after a short time a potash salt crystallises out; this, when acidified, yields an acid, which also gives the violet coloration with ferric chloride. On prolonged boiling with alcoholic potash, however, a neutral body is formed, and only a trace of the above acid. If a solution of this chloride in ether is treated with an ethereal solution of sodium ethoxide, a beautiful yellow sodium compound is precipitated. From these experiments, it would seem

that the compound $C_{18}H_{11}O_3Cl$, is in reality a chlorinated acid of the formula $C_{17}H_{10}OCl.COOH$, and not the acid chloride $C_{17}H_{11}O_2.COCl$, as might be expected from the mode of formation. In the latter case we should expect that dehydrobenzoylactic acid would be regenerated on treating it with water; or on treating it with boiling alcohol or sodium ethoxide, that the ethylic salt of the latter would be formed, reactions which as a fact do not take place. I therefore propose to name the compound $C_{18}H_{11}O_3Cl$, "Chlorodehydrobenzoylactic acid."

Heated by itself in small quantities at a time, it first melts, and then at a high temperature a thick brown oil distils over, which on cooling slowly solidifies, a small quantity of a carbonaceous residue being left. The distillate after washing with a little alcohol melts at $147-149^\circ$, and appears to be the unchanged substance, a proof that it is very stable. Chlorodehydrobenzoylactic acid is easily reduced by warming it with zinc-dust and acetic acid. On adding water, a pale yellowish substance is obtained, which is free from chlorine. After collecting and washing with water, the residue was dissolved in a little hot alcohol, from which it separated on cooling in amorphous flakes. On heating, this substance becomes brownish at about 130° , and melts at between $155-160^\circ$; at a higher temperature carbonic anhydride is given off, and a blackish, tarry residue is left. It dissolves in concentrated sulphuric acid, with a beautiful purple colour, but the solution soon becomes discoloured on standing. It dissolves easily in benzene, and is precipitated in yellowish flakes on adding light petroleum, but as it could not be obtained in crystalline form from these or any other solvents, it was not analysed.

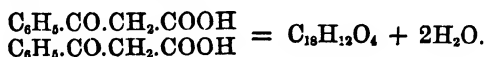
By the action of phosphorous pentachloride on dehydracetic acid, Oppenheim and Precht (*Ber.*, 9, 1100) obtained a compound of the formula $C_8H_5O_2Cl_2$, which is possibly the product of the further action of the above reagent on an unstable body $C_8H_7O_2Cl$, the latter being similarly constituted to chlorodehydrobenzoylactic acid. In order to test this, the action of an excess of phosphorous pentachloride on the compound $C_{18}H_{11}O_3Cl$ was tried, and, as a fact, traces of a second body were obtained, which, however, owing to the small quantity of material at my disposal, could not be further examined.

Constitution of Dehydrobenzoylactic Acid.

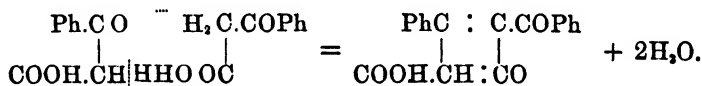
Dehydrobenzoylactic acid, $C_{18}H_{12}O_4$, contains besides a carboxyl-group $COOH$, and a carbonyl-group CO , a fourth atom of oxygen, which, on account of its indifference towards acetic anhydride, reducing agents, and phosphorous pentachloride, can neither be present in the ketone form (CO) nor as hydroxyl, OH , and must therefore be

in the ether form, i.e., joined with its two affinities to two different carbon-atoms, thus; :C.O.C: . It is clear, moreover, that this acid contains two phenyl-groups, otherwise it could not be split up into two molecules of benzoylacetic acid on treatment with alcoholic potash.

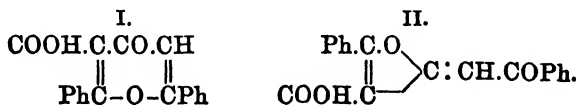
In endeavouring from these facts to establish a formula for dehydrobenzoylacetic acid, it is first important to bear in mind, that it is evidently formed by the elimination of two molecules of water from two molecules of benzoylacetic acid, thus:—



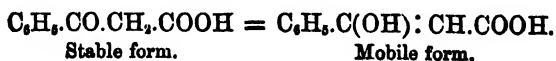
Dehydrobenzoylacetic acid is, however, a monobasic acid, forming salts of the formula $\text{C}_{18}\text{H}_{11}\text{O}_4\text{M}$, so that it follows that the carboxyl-group of one of the molecules of benzoylacetic acid must condense in some way with the second molecule of the latter, one molecule of water being eliminated. This intermediate product then loses a second molecule of water, dehydrobenzoylacetic acid being formed. The simplest way in which this condensation of two molecules of benzoylacetic acid can take place is the following:—



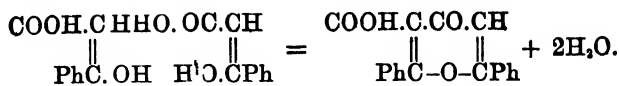
That this formula is not the right one is evident, as it not only contains two ketone-groups, but is so strongly bound together that the splitting up into two molecules of benzoylacetic acid, on simply standing in contact with potash, would be extremely difficult to account for. Besides the above, there are two other possible formulæ for dehydrobenzoylacetic acid, which can be built up on the assumption that the carboxyl-group of one molecule of benzoylacetic acid takes part in the reaction, namely:—



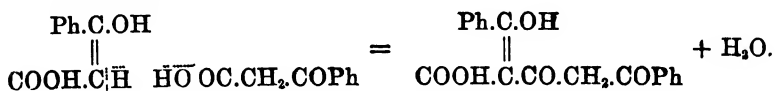
In the formation of these two formulæ, it is necessary to suppose that, as in almost all condensations of ethylic benzoylacetate and acetoacetate, the molecule first undergoes an internal change, thus:—



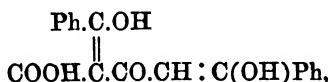
In formula I the condensation takes place between two such mobile forms, thus:—



Formula II is formed in two stages. In the first place, the carboxyl-group of one molecule of benzoylacetic acid (in the stable form) condenses with the second molecule (in the mobile form) in the following way:—

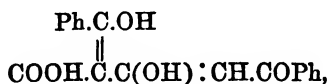


In the second part of the condensation, this intermediate body must be transformed into the mobile form, which can take place in two ways. In the first place, one of the hydrogen-atoms of the CH_2 -group can react with the CO-group next to the phenyl-group, when the following mobile intermediate body would be formed:—

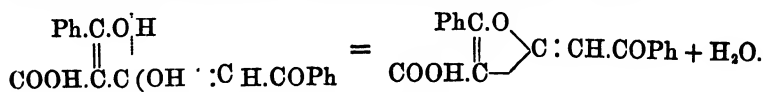


which, on removing the elements of water from the two hydroxyl-groups, gives formula I.

In the second place, the molecular change can take place between the CH_2 -group and the other ketone-group, and thus give the following body:—

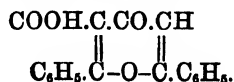


which, on the elimination of water, gives formula II thus:—

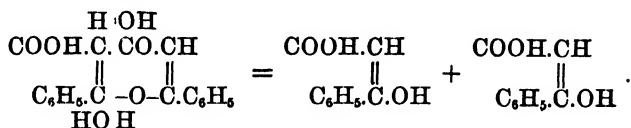


Of these two formulæ, it is evident that, apart from the complicated formation of formula II, formula I is the most likely, as it explains best of all the reactions in which the acid takes part.

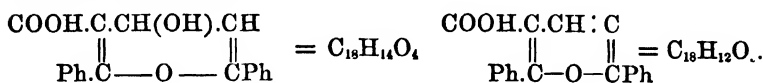
I therefore suggest as the most probable constitution of the dehydrobenzoylacetic acid the following formula:—



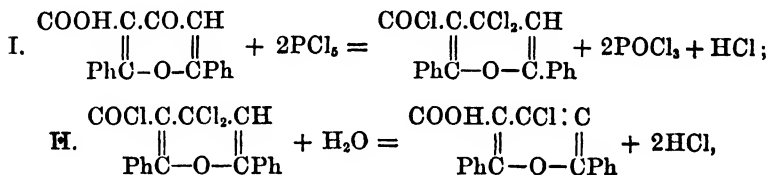
This body is split up on treatment with alcoholic potash into two molecules of benzoylacetic acid, thus:—



The two acids, $\text{C}_{18}\text{H}_{14}\text{O}_4$ and $\text{C}_{18}\text{H}_{12}\text{O}_3$, produced by the action of nascent hydrogen on dehydrobenzoylacetic acid, would therefore have the following formulæ:—



The formation of chlorodehydrobenzoylacetic acid, by the action of pentachloride of phosphorus on dehydrobenzoylacetic acid, undoubtedly takes place in two stages:—



this reaction being in every way analogous to the formation of chlorocinnamic acid by the action of pentachloride of phosphorus on ethylic benzoylacetate as described in Part II (this vol., p. 257) of this research.

On comparing the properties of dehydrobenzoylacetic acid with those of the dehydracetic acid, it is evident that although some minor differences do exist, these two compounds are most probably of an analogous constitution; and as the former is extremely difficult to get in any quantity, I have commenced working on the latter, and hope at some future time to have the honour of laying the results of my experiments before the Society.

XXXIV.—*Presence of Choline in Hops.*

By PETER GRIESS, Ph.D., F.R.S., and G. H. HARROW, Ph.D.

CHOLINE, which is also known under the names of sincaline, neurine, and amanitine, the rational formula of which is $\left. \begin{matrix} (\text{CH}_3)_3 \\ \text{C}_2\text{H}_4.\text{OH} \end{matrix} \right\} \text{N.OH}$, is not only a constantly occurring constituent of several organs of the animal body, for instance the brain, but it has also been proved to exist in some plants. As is well known, it was prepared synthetically by Wurtz, by the action of ethylene oxide on trimethylamine. We have found that it is also present in hops. In order to isolate it from the latter, the following method was adopted. To a concentrated aqueous extract of hops, acidified with hydrochloric acid, a sufficient quantity of a solution of iodine in hydriodic acid was added. In this way a blackish semi-solid precipitate was obtained, which occasionally crystallised in slender shining needles, and no doubt consisted of a choline periodide. Separated from the mother-liquors, and boiled with water, it is converted into the very easily soluble choline iodide, vapour of iodine being at the same time evolved and a tarry mass deposited. The free base is obtained, although at first in a very impure state, by treating the choline iodide with silver oxide, and evaporating the filtered solution on the water-bath. We have found it advisable to purify this crude choline by converting it into the aurochloride, recrystallising this, separating the gold by means of sulphuretted hydrogen, and decomposing the choline chloride thus obtained with silver oxide. The base, freed from water as far as possible by evaporating its solution on the water-bath, forms a thick strongly alkaline syrup, which solidifies in the desiccator to an extremely hygroscopic, crystalline mass; it quickly absorbs carbonic anhydride, has a caustic and somewhat bitter taste, is quite odourless, and is decomposed at a high temperature with formation of trimethylamine. The chloride of the base is also extremely deliquescent, and yields a characteristic platinum-chloride, which is almost insoluble in alcohol, but very soluble even in cold water, crystallising out in fine orange tables.

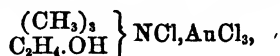
Although the foregoing observations leave little doubt that the base present in hops is, as we have supposed, identical with choline, we have nevertheless submitted its aurochloride to analysis, as it can be very readily obtained in a pure state.

If to a moderately concentrated solution of the base or its chloride, gold chloride be added, the double salt is at once thrown down as a yellow precipitate, which is easily soluble in boiling water and

alcohol, and on recrystallisation from these liquids is obtained in the form of small needles or fine prisms.

- I. 0.532 gram gold salt dried at 100° gave 0.2725 gram CO₂ and 0.158 gram OH₂.
 II. 0.596 gram gold salt gave 0.264 gram Au.
 III. 0.623 gram gold salt gave 0.2757 gram Au.
 IV. 0.3303 gram gold salt gave 0.1465 gram Au.

These numbers agree fairly well with the formula



as will be seen from the following:—

	Calculated.		Found.			
			I.	II.	III.	IV.
C ₄	60	13.54	13.95	—	—	—
H ₁₄	14	3.16	3.32	—	—	—
N	14	3.16	—	—	—	—
O	16	3.61	—	—	—	—
Au.....	197	44.48	—	44.29	44.39	44.35
Cl ₄	142	32.06	—	—	—	—
	<hr/>	<hr/>				
	443	100.00				

Regarding the mode of combination* and the quantity in which choline exists in hops, we are at present unable to give a satisfactory explanation. As to the latter point, however, we may say that, according to the method described, we have not been able to obtain more than about $\frac{1}{10}$ per cent. from the hops.

It was to be expected that choline would also be found in beer, and we have, in fact, succeeded in extracting it therefrom with ease, making use of a method similar to that described above.

Whether the circumstance that choline is present in beer has any physiological significance, is a question which we are not in a position to decide; it is, however, interesting that this never-failing and peculiar constituent of the brain-substance should also be present in one of our most important articles of diet.

* We consider it not improbable that choline exists in hops in loose combination with resin, and that such a combination may form that bitter principle of hops which is easily soluble in water. We have found that a very dilute aqueous solution of choline is capable of dissolving comparatively large quantities of hop resin, thereby producing a liquid of an intensely bitter taste.

ANNUAL GENERAL MEETING,

March 30th, 1885.

Dr. W. H. Perkin, F.R.S., in the Chair.

In bringing before you my Report on the present condition of the Society at the end of my second year of office, I am glad to say that the Society has continued to increase in numbers, and I believe in usefulness. Numerically, however, it has not progressed so rapidly as during the previous year. This arises from two causes—one being that the number of new Fellows elected and paid their admission fees has been somewhat smaller; the second arises from the fact that our losses by death, resignation, and removals, have been exceptionally great. The following tabular statement gives the particulars in reference to our numbers :—

Number of Fellows (Annual General Meeting), March 31st,	
1884	1326
Since elected and paid admission fees	84
	<hr/>
	1410
Deceased	18
Withdrawn	17
Removed on account of arrears	15
	<hr/>
	50
Present number of Fellows	1360
Increase	34
Number of Honorary and Foreign Members at last Annual General Meeting	36
Deceased	4
	<hr/>
Present number	32

From the foregoing statement it will be seen that our losses by death have been large, though not quite so large as in the previous year, but the list contains the names of some of our most valued Fellows. The names are :—G. T. Atkinson; Adrian Blaikie; James Forrest; Robert Harvey; J. W. Hudson; Juwansingji Jaswatsingje; F. M. Jennings; Robert Jones; M. J. Lansdell; James Napier;

H. B. Pritchard; T. K. Rogers; J. L. Shuter; R. Angus Smith; Sidney Gilchrist Thomas; A. Voelcker; Henry Watts; and G. W. Wigner.

Our losses amongst our Honorary and Foreign Members have also been very great. They are:—Victor Dessaignes; Jean Baptiste Dumas; Hermann Kolbe; and Adolph Wurtz.

Obituary notices of these illustrious men will be found further on in this Report, but I may perhaps here draw attention to the fact that two of them became associated with this Society in a particular manner by coming to this country and lecturing before us, and thus many of us were not only privileged to see and hear them, but also to become acquainted with them. The veteran Dumas, it will be remembered, was our inaugural Faraday lecturer, the illustrious Wurtz being one of the subsequent Faraday lecturers.

Amongst our own Fellows we have lost one whom we all miss in an especial manner, as he had been so long officially connected with our Society, and was one of the most important factors in its success, having had the charge of our Journal almost from the first, and carrying it through all its various phases until it attained its present magnitude and importance. We miss him not only on account of his great literary ability and usefulness to us officially as well as to our science at large, but as a friend who will long be remembered for his humility and kindly disposition. I need not say I refer to our late Editor and Librarian, Henry Watts. Owing to his death, it was necessary to appoint a new Editor, and we felt we could not do better than elect to that office Mr. Charles E. Groves, who is so well known, not only for his acquaintance with literature and languages and for his thorough knowledge of chemical science, which he has so often enriched by the papers he has brought before this Society, but also for the experience he acquired in conducting the Journal as Sub-Editor along with Mr. Watts. Mr. Greenaway, who is also well known to most of us, has been appointed to the post vacated by Mr. Groves. As our library has become so much larger than it was, and the duties of Librarian consequently increased, it was thought that the office of Librarian should be made a separate one, and Dr. T. Leonard Thorne has therefore been entrusted with the duties of this post.

Last year I mentioned that a library catalogue was in course of preparation, and that it would probably be completed by about the end of the session. Owing to the death of our Editor this has not been found possible, but we trust that it will not be long before it is ready.

The Library Committee have continued to use their best endeavours to make our library as perfect as possible, and we have to thank

those of our Fellows who have so freely and generously responded to the appeal for copies of old editions of books, &c., to complete our series. The activity of the Committee, and the enormous amount of scientific literature which is published relating to chemistry and allied subjects, is causing some little anxiety as to where the books are to be placed in future. This is a matter which will have to be met before long, as already some of our books have to be kept in rooms not connected with the library.

We have to thank one of our Past Presidents. Dr. De la Rue, who has always shown himself so ready to do anything that will add to the interest of the Society, for the bronze bust of the late Professor Dumas, which has now been placed in the library. It is contemplated placing this, and also that of Professor Hofmann, in more suitable positions than they now occupy.

A number of our country Fellows have felt a want of an official report of the proceedings at our meetings similar to those published by other of the learned societies. The matter was considered by your Council, and it was decided to try the experiment of publishing Proceedings as quickly as possible after the meetings, containing the business transacted, with abstracts or titles of all the papers read, and the discussions upon them. The Honorary Secretaries, with their usual readiness, have undertaken to attend to this matter in the meantime, and I think we must all be pleased with the result. The list of papers on chemical and allied subjects read before the other scientific Societies of the kingdom, which is also given with the Proceedings, is also very valuable. This new publication of the Society when bound up will undoubtedly be found very useful for reference.

It has also been thought that it would be useful to hold receptions by the President and Council in the Society's rooms, of a somewhat informal nature, one in the spring and one in the autumn, so that the Fellows might meet together, and thus interchange of thought would be facilitated, and any Fellow having any objects of special interest might also exhibit them on these occasions. One of these receptions has already been held, and appeared to meet with the approval of the Fellows.

The following is a list of papers read before the Society between March 31, 1884, and March 30, 1885:—

- I. "On the Influence of certain Phosphates upon Vinous Fermentation:" by A. G. Salamon and W. De Vere Matthew.
- II. "On the Occurrence of Rhabdophane in the United States:" by W. N. Hartley.
- III. "On the Influence of Incombustible Diluents on the Illuminating Power of Ethylene:" by Percy F. Frankland.

- IV. "On Trichloropyrogallol:" by C. S. Webster.
- V. "The Synthesis of Galena by means of Thiocarbamide:" by J. Emerson Reynolds.
- VI. "On the Analysis of Woodall Spa:" by W. T. Wright.
- VII. "On the Critical Temperature of Heptane:" by T. E. Thorpe and A. W. Rücker.
- VIII. "On Benzoylactic Acid and some of its Derivatives." Part I: by W. H. Perkin, jun.
- IX. "On the Composition of Coal and Cannel Gas in Relation to their Illuminating Power:" by Percy F. Frankland.
- X. "On Selenium Sulphide." XI. "On the Reaction between Hydrogen Chloride and Selenium Sulphoxide." XII. "On Selenium Seleniochloride:" by E. Divers and Masachika Shimosé.
- XIII. "On Fluorene." Part II: by W. R. H. Hodgkinson.
- XIV. "On a New Form of Pyrometer:" by T. Carnelley and T. Burton.
- XV. "On Refraction Equivalents of Organic Compounds:" by J. H. Gladstone.
- XVI. "On the Estimation of Silicon in Iron and Steel:" by T. Turner.
- XVII. "Note on the Melting Points and their Relations to the Solubility of Hydrated Salts:" by W. A. Tilden.
- XVIII. "A Memoir detailing some Minor Researches on the Action of Ferrous Sulphate on Plant Life:" by A. B. Griffiths.
- XIX. "Note on Ferric Sulphocyanate:" by A. J. Shilton.
- XX. "On β -Naphthaquinone:" by C. E. Groves.
- XXI. "On a Bye-product of the Manufacture of Aurin." Part II: by A. Staub and Watson Smith.
- XXII. "On Calcium Hydrosulphides:" by E. Divers and Tetsukichi Shimidzu.
- XXIII. "The Magnetic Rotatory Polarisation of Chemical Compounds in Relation to their Composition, with Observations on the Preparation and Densities of the Bodies examined:" by W. H. Perkin.
- XXIV. "On the Effect of High Temperatures on Petroleum Hydrocarbons:" by H. E. Armstrong and A. K. Miller.
- XXV. "On the Decomposition of Terpenes by Heat:" by A. W. Tilden.
- XXVI. "A Short Note on the General Law which Governs the Dilatation of Liquids:" by P. de Heen.
- XXVII. "On the Melting Point of Certain Inorganic Substances:" by T. Carnelley and L. T. O'Shea.

- XXVIII. "On Nitrification:" by R. Warington.
- XXIX. "On the Action of Aldehydes and Ammonia upon Benzil" (*continued*): by F. R. Japp and S. C. Hooker.
- XXX. "Isomeric Modifications of Sodium Sulphate:" by U. S. Pickering.
- XXXI. "On some Vanadates of the Amines:" by G. H. Bailey.
- XXXII. "Contributions to our Knowledge of Acetoacetic Acid."
Part I: by J. W. James.
- XXXIII. "On Magnesium Hydrosulphide Solution and its Use in Chemico-legal Cases as a Source of Hydrogen Sulphide:" by E. Divers and T. Shimidzu.
- XXXIV. "On the Origin of Calcium Thiosulphate:" by E. Divers.
- XXXV. "On Some New Paraffins:" by Khan Bahadur Bomanji Sorabji.
- XXXVI. "On Additive and Condensation Compounds of Diketones with Ketones:" by F. R. Japp and N. H. Miller.
- XXXVII. "On the Vapour Pressure of Liquids:" by W. Ramsay and Sydney Young.
- XXXVIII. "On the Action of the Halogens on the Salts of Trimethyl Sulphine:" by L. Dobbin and Orme Masson.
- XXXIX. "Note on the Heats of Dissolution of the Sulphates of Potassium and Lithium:" by Spencer U. Pickering.
- XL. "On the Application of Iron Sulphate in Agriculture, and its Value as a Plant Food:" by A. B. Griffiths.
- XLI. "Notes on the Chemical Alteration in Green Fodder during its Conversion into Ensilage:" by C. Richardson.
- XI/II. "On the Decomposition of Silver Fulminate by Hydrochloric Acid:" by E. Divers and Michitada Kawakita.
- XLIII. "Calorimetric Determinations of Magnesium Sulphate:" by Spencer U. Pickering.
- XLIV. "On Condensation Compounds of Benzil with Ethyl Alcohol:" by F. R. Japp and Miss Mary E. Owens.
- XLV. Note on the Solubility of certain Salts in Fused Sodium Nitrate:" by F. B. Guthrie.
- XLVI. On certain Derivatives of Iso-dinaphthyl:" by A. Staub and Watson Smith.
- XLVII. "Chemico-Physiological Investigations on the Cephalopod Liver and its Identity with the True Pancreas:" by A. B. Griffiths.
- XLVIII. "On the Atomic Weight of Titanium:" by T. E. Thorpe.
- XLIX. "Note on the Constitution of Propylene-chlorhydrin:" by F. Morley and A. J. Green.

- L. "The Action of Zinc Ethide on the Benzoate from Propylene-chlorhydrin:" by F. Morley and A. J. Green.
 - LI. "On Nitrobenzalmalonic Acid:" by C. M. Stuart.
 - LII. "Alkaloids of Nux Vomica. III. Some Experiments from Strychnine:" by W. A. Shenstone.
 - LIII. "The Physiological Action of Brucine and of Bromo-strychnine:" by T. Lauder Brunton.
 - LIV. "Crystallography of Bromo-strychnine:" by H. A. Miers.
 - LV. "On the Formation of Pyridine Derivatives:" By H. v. Pechmann and W. Welsh.
 - LVI. "On Benzoylactic Acid and some of its Derivatives." Part II: by W. H. Perkin, jun.
 - LVII. "On Toughened Filter Paper:" by E. E. H. Francis.
 - LVIII. "The Detection and Estimation of Iodine:" by Ernest Cook.
 - LIX. "A Quick Method for the Estimation of Phosphoric Acid in Fertilisers:" by J. S. Wells, Columbia College.
 - LX. "On the Illuminating Power of Methane:" by Lewis T. Wright.
 - LXI. "On the Conversion of Pelouze's Nitrosulphates into Hypo-nitrites and Sulphites:" by E. Divers and Tamemasa Haga.
 - LXII. "On the Constitution of some Non-saturated Oxygenous Salts, and the Reaction of Phosphorous Oxychloride with Sulphites and Nitrites:" by E. Divers.
 - LXIII. "The Illuminating Power of Hydrocarbons. I. Ethane and Propane:" by Percy F. Frankland.
 - LXIV. "On Benzoylactic Acid and some of its Derivatives." Part III: by W. H. Perkin, jun.
 - LXV. "On the Presence of Choline in Hops:" by P. Griess.
 - LXVI. "On Fluorenes." Part III: by W. R. Heaton Hodgkinson.
 - LXVII. "On the Combustion of Carbon in Dry Oxygen:" by H. Brereton Baker.
- Dr. E. Frankland delivered a lecture on the "Chemical Changes Effected by Micro-organisms:"

The progress of chemistry during the last year has been considerable, and a great deal of interesting and important work has been done, nevertheless it cannot be said to have been a year productive of any very special discoveries. In physical chemistry the subjects connected with heat have occupied a good deal of attention, such as the heat of formation of chemical compounds, &c. Experiments on the liquefaction and solidification of gases by pressure and low tempe-

ratures have also been continued, and in addition to the results which were obtained some time since we now know chlorine not only as a liquid but also as a crystalline solid. The same is true of hydrochloric acid, carbonic oxide, silicon fluoride, and arsenuretted hydrogen.

Last year I referred to the work which was being done with hydroxylamine, and also mentioned that another analytical reagent of equal importance was claiming attention, viz., Emil Fischer's phenylhydrazine; the promise of new work which this substance gave has been fully realized, and it has proved useful not only as an analytical reagent, but has been the means of producing a number of new and important products.

Work is still actively pursued on the pyrroline, pyridine, and quinoline series, and it is remarkable to see how new methods for the production of bodies of this description are being constantly discovered. Those of Behrmann and Hofmann, who obtain pyridine-derivatives from citramide, and of v. Pechmann, who obtains them from malic acid, may be taken as illustrative.

In reference to the pyridine series, it is interesting to notice the experiments of Ladenburg (*Ber.*, 17, 772—774), who finds that the compounds formed by the union of these bases with the iodides of the alcohol radicles when strongly heated yield substituted pyridines in the same way as Hofmann showed some time since that aniline under these circumstances yielded substituted anilines, such as toluidine, &c. Hofmann (*Ber.*, 17, 1200) has also found that conine hydrochloride when distilled with zinc-dust, yields a base he has named conyrine, which he believes to be a propylpyridine or isopropylpyridine, and this by treatment with hydriodic acid at 280—300° regenerates conine which has exactly the same physiological action as the natural (though it is probably optically inactive). Ladenburg (*Ber.*, 17, 1196) has obtained a propylpyridine which when treated with sodium and alcohol yields a base smelling very much like conine; it has many properties in common with conine, and like it is poisonous, acting in the same manner and to the same degree. It is, however, optically inactive, as might be expected. It will be remembered that Schiff (*Annalen*, 157, 352) obtained a base very similar to conine from isobutaldehyde and ammonia some years ago, but it did not appear to agree in all its properties with that body. From this new work which has been done on this subject, we may now soon expect to have the constitution of this base definitely established. Ladenburg has also succeeded in producing piperidine from pyridine. The identity of this product with that obtained from piperine from pepper has been established (*Ber.*, 17, 573—575).

Hofmann while continuing his work on the action of bromine in

alkaline solution on amides, has found the curious fact that nitriles are produced in considerable quantities which contain one atom of carbon less than the amide, in fact, correspond to the amines formed in the reaction, and are in all probability produced from them by the removal of the hydrogen-atoms. As these nitriles can be converted into amides by sulphuric acid, and again treated with bromine and alkali, it is evident that by this means we can gradually work down step by step from one member of the homologous series to another.

It will be remembered that Pechmann and Duisberg (*Ber.*, 16, 2119—2128) succeeded in obtaining substituted coumarins and their hydroxy-derivatives, by acting on aceto- and benzoyl-acetic acids with phenols. Pechmann (*Ber.*, 17, 929—936) has now succeeded in obtaining coumarins by treating malic acid and phenols with sulphuric acid or chloride of zinc, and with ordinary phenol he has obtained coumarin, with resorcinol umbelliferone, and with pyrogallol daphnetin which give all the reactions of the natural bodies.

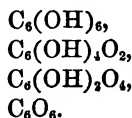
Some very curious results have lately been obtained in reference to the destructive action of aluminium chloride on hydrocarbons. Friedel and Crafts communicated a paper on this subject to this Society in 1882, it has now been further studied by Anschütz and Immerdorff and by Jacobsen (*Ber.*, 18, 657), who have found that this action consists in "a transference of the alcohol radicle from one molecule of a hydrocarbon to another molecule of the same hydrocarbon." Thus toluene yields on the one hand benzene, and on the other xylene and more highly methylated benzenes, ortho-derivatives being very rarely found among the products.

Last year I referred to the discovery of thiophene, or more properly, thiophen, and its homologues by Victor Meyer. During the year our knowledge of this interesting body has been considerably extended, and its preparation rendered comparatively easy. Schulze (*Ber.*, 18, 497) has recently shown that it is contained, as might be expected, in the sulphuric acid used to purify crude benzene, and that if its decomposition be prevented by diluting the acid with an equal bulk of water as soon as it is separated from the benzene, the thiophen, which is doubtless present in the form of a sulphonic acid, may easily be recovered by hydrolysing by merely passing steam into the acid liquid.

The synthesis of thiophen recently effected by Volhard and Erdmann (*Ber.*, 18, 454), by merely distilling sodium succinate with phosphorus trisulphide (by which about 50 per cent. of the theoretical yield is obtained), is also of interest, as well as the production of methylthiophen from sodium pyrotartrate by the same reagent. The methylthiophen, however, appears to be isomeric with that separated from coal-tar toluene by Victor Meyer. According to Volhard and

Erdmann, thiophen when cooled in a mixture of carbon dioxide and ether crystallises like benzene. Paal's synthesis of methylphenylthiophen from acetophenoneacetone and of thiophencarboxylic acid—which is easily resolved into carbon dioxide and thiophen—from mucic acid may also be referred to here.

One of the most interesting of recent researches is that of Nietzki and Benckiser on hexhydroxybenzene, $C_6(OH)_6$ (*Ber.*, **18**, 499), which they have succeeded in obtaining from nitranilic acid (dinitrodihydroxyquinone). They find that the diamido-body obtained from this when treated with nitric acid yields a product of the composition $C_6H_{16}O_{14}$, which when treated with reducing agents yields this substance. They also find that when treated with concentrated nitric acid, hexhydroxybenzene is reconverted into the body having the remarkable formula $C_6H_{16}O_{14}$. This decomposes when heated to 100° , or when boiled with water, carbon dioxide being given off, and on adding potash solution to the residue or the boiled solution, orange-yellow needles of a potassium salt of the formula $C_6K_2O_6$ are obtained, which they have identified as potassium croconate, and they believe that the bodies obtained by Lerch (*Ann. Chim. Pharm.*, **124**, 20), from the compounds of potassium carbonic oxide (formed during the preparation of the metal) were hexhydroxybenzene, tetrahydroxyquinone, and the compound $C_6H_{16}O_{14}$, and in fact that the compound $C_6(OK)_6$ is present in "potassium carbonic oxide." From experiments on the remarkable substance $C_6H_{16}O_{14}$, they came to the conclusion that it is a compound of $C_6O_6 + 8H_2O$, and a quinone which they call triquinoylbenzene. This appears to be confirmed by the production of the intermediate hydroxy compounds, the following being the series of products:—



In reference to agricultural chemistry, Messrs. Lawes and Gilbert have contributed a most important and interesting paper to our Society, 1884, p. 305—407, on the ash of wheat-grain and wheat-straw. They give the analyses of no less than 92 wheat-grain and wheat-straw ashes, every ash being of produce of known history of growth as to soil, season, and manuring; all the specimens having been grown at Rothamsted. Out of the many important deductions this paper contains, the following are extremely interesting. It appears in reference to the grain that on the whole there is great uniformity in its mineral composition under different conditions of manuring, provided only it is perfectly and normally ripened, the

influence of season producing a much wider range in the mineral constituents of the grain than the manuring. This, however, is not the case with the straw, as it is found that the amount of mineral ash constituents in the straw, and therefore in the total crop, have a very direct connection with the amounts available in the soil, but the amounts stored up in the grain itself are little influenced by the quantity taken up.

Besides the researches just referred to, there has been a considerable amount of good work done, but it would be out of place for me to enter into it more fully in this short review.

Last year I took occasion to draw attention to the comparatively small amount of original work which was being prosecuted in this country, notwithstanding the increased number of laboratories, and the greater facilities which existed for the encouragement of research. It will be seen from the list of papers that the number brought before the Society during the past year has not increased, but if the papers themselves are examined, I think we shall find that the amount of work done is somewhat larger—though certainly not so large as it should be—and it is to be hoped that the spirit of research will be stimulated in the laboratories of the kingdom, and that men may be turned out, who are not only more or less analysts, but thorough chemists. Let us not be contented with looking back with pride to what our ancestors have done, but let us follow their example.

VICTOR DESSAIGNES, the third son of Jean Philibert Dessaignes, was born on the 30th December, 1800, in the College of Vendôme, where he was educated. He afterwards came to Paris and was made an advocate at the age of 21, but soon turned aside from this and entered the École de Médecine. Here he acquired a veritable passion for chemistry, and on taking his degree as Doctor of Medicine in 1835, his thesis was on the effect of various chemical agents on the human body. Appointed *receveur municipal* of his native town, he devoted all his spare time and resources to the study of chemistry, publishing numerous papers on original organic research.

In 1861 the Academy presented him with the Jecker prize; in 1863 he was made Chevalier of the Legion of Honour, and in 1869 he was elected correspondent of the Academy in the place of Schoenbein. During the last twenty years of his life he relinquished all chemical pursuits.

He had an attack of bronchitis in December of 1884, and appeared to have entirely recovered from its effects, but on the 4th of January, 1885, he was seized with syncope, and died suddenly at the advanced age of 84.

His chemical work was varied, and included some of the most important results obtained at that time in the synthesis of organic compounds. It was he who first noticed the decomposition of hippuric acid into benzoic acid and glycocine, and subsequently prepared hippuric acid by synthesis. He also synthesised aspartic acid from ammonium malate, and changed malic acid into succinic acid, and tartaric acid into malic acid. He was the discoverer of tartronic and malonic acids, and investigated the nature of several of the organic compounds which occur ready formed in plants.

JEAN BAPTISTE ANDRÉ DUMAS was born at Alais, in the Department of the Gard, July 14, 1800.

The little town of Alais was almost unknown at the beginning of this century, but at the college there, which had then no lack of pupils, he received his early education, more especially in Latin, so congenial to the classical traditions of the neighbourhood.

Although these associations had a tendency to direct the mind of young Dumas to the study of the past, there were other influences, not less potent, continually calling him back to the present. Indeed, the town of Alais, by its unique situation, afforded excellent opportunities of observing nature and the processes of adapting her products to the use of man. Both in his speeches and writings he frequently refers with gratitude to these varied impressions of his early youth at Alais.

It would be difficult to imagine a happier complement to a classical education than the lessons taught at every step in this delightful country. Nor were they lost on young Dumas, who at fourteen years of age had acquired a rudimentary knowledge of natural science, in addition to his attainments in classical literature. Having made up his mind to enter the Navy, he might at once have presented himself for examination, but for an insufficient acquaintance with some branches of mathematics. While Dumas was still preparing for his naval examination, the political events of 1814-15 obliged his family to renounce this project and to select a career for the youth which would entail less sacrifice.

Dumas accordingly entered as apprentice at an apothecary's in Alais. This position, in which he pursued his studies, did not afford much opportunity for acquiring scientific knowledge, and the young man became soon impressed with a strong desire to give up this place and to quit his native town.

Soon after, in 1816, Dumas travelled on foot from Alais to Geneva, where there were lectures on botany by M. de Candolle, on physics by M. Pictet, and on chemistry by M. Gaspard de la Rive. He had, besides, the superintendence of a tolerably large laboratory, belonging

to the pharmacy of Le Royer, and formerly used for the courses of applied chemistry given by M. Tingry.

The pharmaceutical students, who frequently united in botanical excursions during the summer, started the idea of winter meetings for scientific studies. Seeing that Dumas had a laboratory at his disposal, it was suggested that he should give them a course of experimental chemistry. This was his *début* in the professorial career.

Meanwhile Dumas had become introduced to De la Rive, to De Saussure, and to De Candolle, and each of these in his way began to take a warm and lasting interest in him; they encouraged his studies, and assisted him to the best of their powers in his pursuits. It was most likely at the instigation of his new friends that Dumas, reviving his early naval predilections, began seriously to think of, and to prepare for, an exploring expedition to some distant part of the world. A monograph on the Gentianæ, chiefly written for the purpose of becoming familiar with the language and the ideas of botanical science, was a fruit of these aspirations.

But this was not to be his mission. Biot's great treatise, which for half a century was to remain the standard text-book on physics, had just appeared, and Dumas found, more especially in the first volume, much to direct his attention to experimental work. At the same time he studied with indefatigable zeal the works of Lavoisier, and the "Statique Chimique" of Berthollet.

Dumas was then eighteen years of age. It was about that time that he had the good fortune to make himself useful to one of the principal physicians of the town, a circumstance which contributed not a little to advance him in the circles in which he had hitherto lived. Dr. Coindet asked him to examine some carbonised sponges, and to ascertain more especially whether iodine was present in them. Having after some days received an affirmative answer, Dr. Coindet no longer hesitated to consider iodine a specific against goitre. Dumas was then asked to give his attention to the subject and to point out the preparations in which iodine might be most conveniently administered. He suggested tincture of iodine, potassic iodide, and iodised potassic iodide. Soon afterwards these new remedies were mentioned in a German journal published at Zurich, and it is in this connection that the name of Dumas is first met with in scientific literature.

About this time Dr. J. L. Prévost, after an absence of several years, returned to Geneva. He had long been resident in Edinburgh and Dublin, and amongst his studies was an examination of the physiological effects of digitalis; he was naturally anxious to obtain the active principle of the plant, and invited Dumas to join him in this inquiry. The attempts to isolate this principle, however, did not lead

to any result. But however unsuccessful, these joint labours gave rise to a far more fruitful collaboration.

Whilst studying together the physiology of Richerand, a work then in great repute, and the memoirs of Magendie, which were beginning to attract increased attention, the two friends resolved to engage in a series of chemico-physiological researches. It seemed natural enough to commence by a renewed study of the blood, and they were soon able to publish a paper on this subject in the *Bibliothèque Universelle de Genève*, and in the title Dumas still figures as *Elève de Pharmacie*.

It was about this time that the death of Princess Charlotte had excited a feeling of sorrow all over Europe. The pathological problem presented by this sad event induced the two experimentalists to resume the study of the transfusion of blood. A very important result of their investigations was to show that urea is present in the blood of animals from which the kidneys had been removed. They inferred from this that the function of the kidneys is not to produce but to eliminate urea formed in the blood.

From the researches on blood Prévost and Dumas proceeded to the examination of the phenomenon of fecundation, the knowledge of which they considerably expanded.

Prévost and Dumas' suggestion as to the treatment of stone by electricity should not be left unnoticed. Their experiments showed that the current of a powerful battery is capable of destroying and dissolving the phosphatic calculi of the bladder, without its mucous membrane being materially affected. Although, at a subsequent period, these researches were continued and materially enlarged by the late Dr. Bence Jones, the treatment indicated does not seem to have been successfully applied in surgery.

In 1822, Dumas might have settled at Geneva, and many circumstances led him to think seriously of doing so. An incident, however, which happened at that time induced him within a few days to change his mind. He made the acquaintance of Alexander von Humboldt, who invited him to be his companion during a few days' stay at Geneva. The short intercourse with this extraordinary man suddenly expanded his aspirations.

He was so impressed with what he told him of Parisian life, of the happy collaboration of men of science, and of the unlimited facilities which the French capital offered to young men wishing to devote themselves to scientific pursuits, that he began to think that Paris was the only place where he might hope to find the advice and assistance which would enable him to carry out the labours over which he had been pondering for some time. His mind was soon made up—he must go to Paris.

Dumas' removal to Paris, which took place in 1823, brought the

physiological labours in which he had been engaged along with Prévost to a conclusion. Though the separation from his friend must have been deeply felt by the young *savant*, he had the good fortune to become acquainted with three young men of about his own age, with whom he soon entered into friendly alliance. These were Victor Audouin, the zoologist, well known even at that time, Adolphe Brongniart, who had already published several important botanical papers, and Henri Milne Edwards, who had just terminated his medical studies and was working for his degree. The friendship of these three men, subsequently strengthened by family ties, has ever been looked upon by Dumas as one of the most important acquisitions of his life.

If a legitimate desire to become acquainted with the leading men of science of that day was one of the principal motives in determining Dumas to leave Geneva, his wishes were gratified far beyond his most sanguine expectations. Nothing could have surpassed the kindness with which the young aspirant was received by the very men to whom he had hitherto been looking up with mingled sentiments of reverence and awe. Indeed, a most kindly feeling of good fellowship towards youthful workers in the same field of inquiry was a noble feature in the character of nearly all men of science of that period. La Place, Berthollet, Vauquelin, Gay-Lussac, Thénard, Alexandre Brongniart, Cuvier, Geoffroy Saint Hilaire, Arago, Ampère, Poisson, all gave striking proofs of their desire to smooth the path of young investigators, and thus to promote the advance of science.

The place of Répétiteur de Chimie to Thénard's course of lectures in the École Polytechnique having become vacant at that time, Arago proposed Dumas for the office, and he was elected by the council of the school before he was aware that he was a candidate. There was at that period in Paris an establishment for evening lectures on literature and science, resembling in a measure the Royal Institution of Albemarle Street, although the literary element predominated. The chair of chemistry at that institution, often called Lyceum, but better known by its later name of Athenæum, had become vacant, and Ampère succeeded in procuring the appointment for Dumas without having previously spoken to him on the subject.

From this moment, owing to the influence of his two illustrious protectors, the study of physiological problems receded more and more in the background, whilst all his energy was directed towards chemical science.

Still many circumstances conspired which prevented Dumas from engaging much in scientific researches during the first years of his stay in Paris. His lectures at the Athenæum required a great deal of preparation; he was, moreover, in his capacity as assistant to

Thénard's course at the École Polytechnique, assiduously practising the art of experimenting in public, in which he soon attained the highest skill. At the same time he founded (in 1824), with his friends Audouin and Brongniart, the "*Annales des Sciences Naturelles*," and also began to collect the materials necessary for the publication of his grand "*Traité de Chimie appliquée aux Arts*," the first volume of which appeared in 1828.

But if this period was for Dumas one of incessant labour, and often of the most strenuous efforts, it also enabled him to realise the most ardent of his aspirations. For some time Dumas had been intimate with the family of Alexandre Brongniart, the father of his friend Adolphe, and was not long before he became betrothed to Mdlle. Herminie Brongniart, the eldest daughter of the illustrious geologist. It was on February 18, 1826, that the matrimonial alliance was concluded which for more than half a century was a source of the purest happiness.

At the very commencement of his labours in the cause of organic chemistry, Dumas found himself face to face with a powerful rival in Germany, who, setting out by a curious coincidence from the same starting-point, the study of pharmacy, had entered the lists without passing through the physiological and natural history stages like his competitor. Liebig and Dumas have had, indeed, some strange encounters on the field of science. These were occasionally rather violent; but however fierce the aggression, the combatants never forgot that they were both fighting under the banner of truth, and the contest having been decided, the antagonists invariably separated with increased regard for each other.

But we must return to Dumas' early labours in the field of experimental investigation. They were by no means exclusively devoted to organic chemistry; indeed, one of his first researches, which riveted at once the eyes of the scientific world upon the young French chemist, was of a much larger scope. We allude to the classical paper, "*On some Points of the Atomic Theory*," which was published in the "*Annales de Chimie et de Physique*" for 1826. Whoever to-day, after a lapse of nearly sixty years, peruses this admirable memoir, will find that many of our modern views, which we are in the habit of considering as the acquirement of the last few decades, had already found expression in this paper.

In glancing back at the results of this memoir in the light of our present views, we perceive at once what a start the French chemist had gained on his contemporaries. "I am engaged in a series of experiments," he says, "intended to fix the atomic weights of a considerable number of bodies, by determining their density in the state of gas or vapour. There remains in this case but one hypothesis to

be made, which is accepted by all physicists. It consists in supposing that in all elastic fluids observed under the same conditions, the molecules are placed at equal distances, *i.e.*, that they are present in them in equal numbers."

It is obvious that the author opens his inquiry with the very conceptions which form the basis of our present views in chemical philosophy; and it is only to be wondered at that the happy enlistment of Avogadro's ideas into the service of chemistry, which we owe to Dumas' initiatory sagacity, should for more than a quarter of a century almost have fallen into oblivion.

Having premised the general scope of his inquiry, Dumas proceeds to describe his well-known method of taking vapour-densities. Amongst the numerous results in Dumas' paper we may mention that the determination of the vapour-density of chloride and fluoride of silicon established the view now held regarding the constitution of silicic acid, thus overthrowing the old formula of this compound upon which Berzelius had based his classification of silicious minerals.

There were other experimental researches of importance carried out by Dumas about this period. It had long been his intention to resume the study of the ethereal salts; and, in conjunction with Boullay, he made an elaborate investigation of nitrous, acetic, benzoic, and oxalic ethers. The composition of these substances was finally settled by accurate combustions and vapour-density determinations, and then experiments on the saponification of these compounds formally established their nature.

These investigations led to others, amongst which, those on the formation of oxamide, or chlorocarbonic ether, and on urethane may be specially mentioned. Here, also, the splendid papers on wood-spirit and spermaceti, jointly published by Dumas and Peligot, deserve to be noticed, although they belong to a somewhat later period.

While these experiments were still going on, a strange incident directed the attention of Dumas to a perfectly different order of phenomena, the study of which occupied him for many years of his life, and ultimately led him to one of his finest conceptions, the theory of substitution. It is not generally known that it is to a *soirée* at the Tuileries that the origin of the substitution-theory must be traced. One evening the visitors at the palace were greatly incommoded by irritating vapours diffused throughout the apartments, and obviously arising from the wax candles burning with a smoky flame. Alexandre Brongniart, in his capacity of director of the porcelain manufactory at Sèvres, was looked upon as chemist to the king's household, and it appeared but natural that he should be consulted respecting this unpleasant incident. Brongniart intrusted his son-in-law with the

task of investigating the suspicious candles, and Dumas was all the more inclined to engage in this inquiry, that he had already made some experiments in that direction, having been asked by a merchant to suggest a method of bleaching certain kinds of wax which resisted the ordinary processes, and thus remained unsaleable. Nor had Dumas any difficulty in supplying the explanation. The irritating vapours were hydrochloric acid, and it was thus obvious that the candle manufacturer supplying the palace had made use of wax bleached with chlorine, and that the chlorine-bleached wax had retained chlorine, which during the combustion of the wax was evolved in the form of hydrogen chloride. It was proved by experiment that organic substances when treated with chlorine retain it in combination, and a new field of investigation was thus opened, which within a comparatively short time yielded a harvest of interesting results.

It is well known that the researches suggested by the experiment above mentioned led to the view of chlorine being capable of displacing hydrogen, atom for atom, in organic compounds.

This view, diametrically opposed to the dualistic conception of the electrochemical theory of the time, was vehemently contested by Berzelius and his school, who exhausted the resources of argument, scorn, and even ridicule against them. Nevertheless, Dumas' ideas rapidly took root, and an impetus was given to the movement when it was joined by Laurent, who by his unremitting researches assisted more perhaps than any other chemist in the propagation of the theory of substitution.

Excellent illustrations of substitution are furnished by Dumas' work on olefiant gas and ordinary ether, and also by his examination of the action of chlorine on alcohol; although in this instance he was forestalled by Liebig, who by his researches had been led to the discovery of chloral and chloroform. But if Dumas lost the discovery of these two compounds, he had at all events the satisfaction of establishing their true composition, and of thus supplying the key to the correct interpretation both of the formation of chloral from alcohol and of its decomposition by alkalis into formic acid and chloroform.

But the inquiry which more perhaps than any other has contributed to establish Dumas' ideas in the minds of chemists is his investigation of the action of chlorine on acetic acid. The trichloroacetic acid formed in this reaction retains all the characteristic properties of the original compound, its metallic and ethereal salts resemble those of acetic acid, and when Berzelius and the champions of dualistic views still endeavoured by constrained interpretation to prove acetic and chloroacetic acid to differ in constitution, Dumas showed that even their metamorphoses are strictly analogous.

Among the numerous researches undertaken with a view of eluci-

dating the theory of substitution, the joint inquiry of Dumas and Stas on the action of alkalis on alcohols and ethers must not be forgotten. They prove that the alkalis act as oxidising agents, hydrogen being evolved, with simultaneous formation of the acids corresponding with the alcohols. Amylic alcohol, then just brought to light by Dumas and Cahours' researches, is thus found to yield valeric acid, up to that time obtained only from *Valeriana officinalis*.

A few years later Dumas returned once more to the acids generated by the oxidation of the alcohols. But what on this occasion fixed his attention was the simple relation in which these acids stand to each other. For the first time, indeed, we hear of the series of fatty or aliphatic acids. The observations recorded by Dumas have greatly contributed to develop the classification of organic compounds in homologous series. A very important series of this kind was indicated by Dumas when, on this occasion, he showed that between formic and margaric acids not less than fifteen acids could be assumed to exist, differing from one another by a constant elementary difference, CH_2 , of which nine at least were known at that time.

The number of elements in organic compounds being so very limited, it was but natural that from the very first considerable attention should have been bestowed upon the quantitative analysis of these substances; and that we find the very chemists who laid the foundation of organic chemistry also engaged in elaborating the methods for determining the organic elements. There are, indeed, no two chemists to whom we are more deeply indebted for the growth of our methods of analysing organic substances than Liebig and Dumas, and their names remain associated with the processes they have introduced. We speak of Liebig's method of estimating carbon and hydrogen, and of Dumas' process for determining nitrogen.

In relation to the determination of the composition of organic substances, the revision of the atomic weight of carbon by Dumas and Stas may be alluded to, the number they found being 12 instead of 12.24, that adopted by Berzelius. This investigation will ever be looked upon as a model for experimental researches, and their atomic weight of carbon, although it has undergone a trifling modification by subsequent researches, has since been universally adopted.

This inquiry naturally led to a revision of the atomic weight of oxygen. Experiments made by Dumas on a scale not hitherto attempted, consisting in the reduction of large quantities of oxide of copper, showed the volume weight of oxygen to be exactly 16, referred to hydrogen as unity.

The correctness to which the experiments previously mentioned had led, as regards the composition of carbonic acid and water, suggested also a re-examination of atmospheric air. Dumas undertook this

investigation in conjunction with his friend Boussingault, the results being :—

	By weight.	By volume.
Oxygen	23	20·81
Nitrogen	77	79·19
	<hr/> 100	<hr/> 100·00

The rectification of the atomic weight of carbon and the inquiries more immediately connected therewith must be looked upon as the prelude of Dumas' long series of researches on the atomic weights of the elements. They were mostly published at a later period (from 1858 to 1860). They embrace not less than thirty elements, or about one-half of those then known; and the number of experiments made for the purpose of fixing their atomic weights is nearly 200.

Among the researches carried out by Dumas in conjunction with other chemists we have still to notice those with Malaguti and Leblanc on the transformation of the ammoniac salts and amides into the alcohol cyanides (nitriles), those with Cahours on the composition of the neutral nitrogenous substances in the vegetal and animal organism, and those with Milne Edwards on the conversion of sugar into fat (wax) within the organism of the bee.

The last experimental inquiries published by Dumas are his researches on alcoholic fermentation (1872), and an interesting paper on the occlusion of oxygen in silver, which appeared as late as 1878.

Lucidity of exposition and grace of style are not necessarily associated with the gift of successfully interrogating nature. It happens but too frequently that the results of admirable inquiries are almost hidden in papers hastily, not to say negligently, written. But no one ever found fault with Dumas in this respect. Few chemists, perhaps, published their researches in a more attractive and lucid form. And the same graceful elegance and perspicuity of style are found in whatever proceeded from his pen. One might fancy that he took the same pains whether it was a friendly letter or an elaborate report, a festal oration or a philosophic essay that he was writing.

The works of Dumas present considerable variety, both as to the subjects discussed and to the form of treatment adopted. We may here briefly allude to his more important writings.

Among these, his "*Traité de Chimie appliquée aux Arts*" deserves to be noticed first. This important work is in eight volumes, the first of which appeared in 1828; the last one twenty years later. It is accompanied by a fine Atlas of Plates. In the preface, the author informs us that the book is founded on the notes collected for a course of chemical technology extending over three years, which he had to

deliver at the Royal Athenæum. And nothing could give a better idea of the time and energy devoted to the preparation of these lectures.

About ten years after the first volume of the "*Traité de Chimie appliquée aux Arts*" had appeared, Dumas' celebrated "*Leçons sur la Philosophie Chimique*" were published. In these eleven lectures, which, during the summer of 1836, were delivered in the College of France, he traces the development of chemical doctrines from remotest antiquity up to the time at which the course was given. Indeed, the last lecture is devoted to the generation of electricity by chemical action, to the chemical effects of the battery, to the ever-memorable experiments of Sir Humphry Davy, and to the electro-chemical theory he founded thereon, as well as to the electro-chemical theories of Ampère and Berzelius; while it concludes with a survey of Faraday's electrolytical researches.

Among the numerous writings of Dumas none, perhaps, has found a more cordial reception in wide-spread circles than the lecture with which on August 23, 1841, he concluded his course of chemistry in the Medical School of Paris. This lecture, published under the title "*Essai de Statique Chimique des Êtres Organisés*," par MM. Dumas et Boussingault, gives in a simple form the principal features of the life of plants and animals considered from a chemical point of view, presenting a most eloquent *résumé* of the chemical and physiological researches in which the two friends, either individually or jointly, had been engaged for many years.

The publication of this lecture gave rise to a dispute between Dumas and Liebig regarding the priority of the ideas propounded therein. The great German chemist having but a year previously, in 1840, published his celebrated work, "*Organic Chemistry in its Application to Agriculture and Physiology*," had been naturally led to investigations of a similar order concerning the chemical phenomena of animal life, and was then actually preparing his "*Chemistry applied to Animal Physiology*." Liebig, no doubt, had freely stated the results of his researches in lectures delivered long before the publication of Dumas and Boussingault's pamphlet; but there is not a shadow of proof that Dumas was influenced by inquiries which at the time were not published. The accusations, it cannot be denied, rather hastily hazarded by Liebig, could not but cause a temporary estrangement between the two great chemists. Fortunately it was of only short duration, and left no bitterness in their minds. The un-biassed reader of to-day no longer doubts that the conceptions which formed the subject of dispute were independently arrived at by both inquirers. And this view is confirmed when we learn that documents have since been found which unmistakably prove that as far back as

1792 Lavoisier was acquainted with the mutual relation presented by the phenomena of vegetal and animal life.

The important series of commemoration addresses which Dumas delivered on many of his departed friends and colleagues, not only give a life-like portrait of the person commemorated, but contain numerous interesting particulars which, drawn from the author's own personal intercourse with his heroes, give a life-like colouring to the memoirs. Such commemoration addresses Dumas has delivered on Auguste Béroet, Jules Pelouze, Geoffroy Saint-Hilaire, Auguste de la Rive, Alexandre and Adolphe Brongniart, Guizot, Antoine Balard, Count Rumford, Victor Regnault, Charles and Henri Sainte Claire-Deville.

Nor should his beautiful Faraday lecture be left unnoticed. It is well known that soon after Faraday's death in 1867 the Council of the Chemical Society of London organised a periodical celebration of his life and labours by instituting a triennial prize to be conferred upon scientific men of all countries whom they proposed from time to time to invite for the purpose of rendering homage to the memory of the great experimental inquirer of our century. It was Dumas who, on June 17, 1869, opened this cycle of commemoration addresses by delivering a most eloquent lecture in the theatre of the Royal Institution, where the voice of Faraday himself had been so often heard.

Essentially different from these commemoration addresses, but not less masterly of their kind, are the numerous orations he delivered—sometimes in the name of the Academy, sometimes in his capacity as Vice-President of the Educational Council—at the funeral obsequies of distinguished men, amongst which those on Elie de Beaumont (1874), on Le Verrier (1877), and on Claude Bernard (1878), may be specially mentioned.

But there were other duties than the delivery of commemoration addresses in store for the academician. Any task imposed upon the Institute in the accomplishment of which chemistry was directly or indirectly concerned, invariably devolved upon Dumas.

The "Comptes Rendus" of the last fifty years contain an endless series of reports addressed to the Academy, which, on a great variety of subjects, either alone or in conjunction with some of his colleagues, he drew up. Some of these reports are elaborate essays, the interest in which will not die with the ephemeral conditions of their origin. Among them, those on Nicolas Leblanc and the early history of the soda-process, on the diseases of the silkworm, on the devastations of the phylloxera, may be quoted as illustrations.

We have still to allude to some literary achievements of another character. It has been already stated that in 1824 Dumas founded, in conjunction with his friends Audouin and Adolphe Brongniart, the

"*Annales des Sciences Naturelles*." At a later period, in 1840, he became one of the editors of the "*Annales de Chimie et de Physique*," an office which he held up to his death. He has thus been an editor of that journal for upwards of forty years, but his contributions to it extend over more than half a century.

The lectures at the Athenæum, together with the literary engagements which they had occasioned, his duties as Répétiteur at the École Polytechnique, and the experimental researches continued without interruption, would have left but little leisure to any man of ordinary energy. Dumas, however, found time for additional work. Well aware of the imperfection of scientific instruction for technical purposes in the then existing institutions of France, he conceived the idea of establishing, in conjunction with his friends Théodore Olivier and Eugène Péclet, a school intended to supply the defect. The new school, which assumed the title of "École Centrale des Arts et Manufactures," was opened in 1829.

At first Dumas lectured at this school on general, analytical, and industrial chemistry. At a later period, when its financial position permitted the appointment of additional chemical teachers, he confined himself to either one or other of these branches. The lectures on general chemistry he continued up to 1852, when he resigned in favour of Cahours.

The number and variety of lectures which Dumas had to deliver at the École Centrale immediately after its opening, in addition to his duties at the Polytechnic School, rendered it an absolute necessity for him to diminish his engagements elsewhere, so as to enable him to find time for the various researches he had then in hand. Nor did he hesitate (in 1829) to retire from the Professorship at the Royal Athenæum, to which Bussy was then appointed. The alleviation thus obtained was not of long duration. In 1832 Guy-Lussac resigned his chair at the Sorbonne, which, like a natural inheritance, fell to Dumas; and to this position, which he held up to 1868, when Henri Ste. Claire-Deville, after having acted as his substitute since 1853, became his successor, was soon added another important appointment. For, when (in 1835) Thénard withdrew from his Professorship at the École Polytechnique, the duties of the office devolved upon Dumas, who for twelve years had been a Répétiteur at the School. Dumas was, in fact, appointed, and remained in connection with the Institution up to 1840, when he resigned in favour of Pelouze. The list of his Professorial appointments, however, is not yet exhausted. After the death of Deyeux (in 1839) he was induced, chiefly by Orfila, to undertake the duties of the Chair of Chemistry in the École de Médecine.

In these several positions, Dumas had to lecture on very different

subjects: he had, moreover, to shape his courses according to the traditions of the places in which he lectured, and to adjust them to the different ages, acquirements, and wants of the students he addressed. His unprecedented success as a lecturer is unequivocally proved by the lively and lasting recollections which his lectures, addressed to such a diversity of audiences, have left in the minds of his hearers. Even those who have had the good fortune of attending but a single one of his lectures will ever remember the clearness and precision of his reasoning and the attractive grace of his delivery.

But it was by no means only in lectures that Dumas has sown broadcast the seeds of chemical science. He was, in fact, the first in France to adopt that efficient system of laboratory teaching so happily inaugurated by Liebig, which has ever since been a prominent feature of the German Universities. The laboratory which he had established in the École Polytechnique, though well adapted for an experimental inquirer working along with his assistant, was altogether unfit for the reception of a number of pupils. That he might be able to associate with experimental students, he founded, as early as 1832, a laboratory of research at his own expense.

Almost immediately after the Revolution of February, new labours of the most diverse kind began to encroach upon Dumas' scientific work. The political and social upheaval of 1848, shaking, as it did, the stability of all French institutions, turned into political and administrative courses many men of mark whose energies had been hitherto exclusively devoted to the service of science. It would have been strange, indeed, had not the want been felt of securing Dumas' well-tried powers for the public affairs of the country. Election to the National Legislative Assembly, appointment as Minister of Agriculture and Commerce, admission to the Senate, President of the Municipal Council of Paris, and nomination as Master of the Mint of France, are the steps by which he rapidly rose in his new career.

With the fall of the second Empire the political and administrative career of Dumas came to an abrupt termination. The Senate had ceased to exist, and in the stormy days which followed, the Municipal Council had naturally changed its composition; and even in the Mint, where his rich experience and his rare talent of organization might have been still of such use in the public service, the man who played so conspicuous a part under the Imperial Government was displaced.

Having thus withdrawn from his official positions, Dumas found himself at the age of seventy in the possession of *otium cum dignitate*; but he never allowed himself to enjoy it in any other than the Ciceronian acceptation of the words. After his retirement from political and municipal life Dumas once more exclusively belonged to science. There was no chemical aspiration which he was not anxious to assist,

no problem in the domain of chemistry, physics, or physiology to the solution of which he was not happy and proud to contribute, no scientific movement of any kind to the furtherance of which he was not willing to open the treasury of his matured experience or to lend at least the prestige of his name. But he was never more happy than when, in furthering science, he was at the same time able to serve the material wants and to promote the well-being of his fellow-citizens.

That to scientific services continued for upwards of half a century science should have accorded with unstinted hand a rich share even of her external marks of honour was but to be expected; no Academy, no learned Society but has deemed it an honour to inscribe the name of Dumas on its register. A member of the French Institute at the early age of thirty-two, he has in due time reaped the full harvest of distinctions in store for successful cultivators of science. He became a correspondent of the Berlin Academy of Science in 1834, and a Foreign Associate of that body in 1880; he was elected a Foreign Member of the Royal Society of London in 1840. He was an honorary member of the English, French, and German Chemical Societies; these associations, the second of which originated in Dumas' laboratory, elected him as a matter of course immediately after their institution. In 1843 the Royal Society awarded to him the much-coveted Copley Medal. That he was the first to obtain the Faraday Medal in the gift of the Chemical Society of London, has been already mentioned. Dumas was a Knight of the Prussian Order *pour le Mérite*, the highest scientific honour Germany can bestow, and it may further be added that he received the Grand Cross of the Legion of Honour, and was a Knight of a goodly number of other Orders in Christendom.

In the autumn of 1883 Dumas' health, which up to that time had been unimpaired, began to fail. By the advice of his physicians he passed the winter in the south of France. He died at Cannes on the 11th of April, 1884.

ADOLPH WILHELM HERMANN KOLBE was the son of a Lutheran clergyman, and was born on September 27, 1818, at Elliehausen, near Göttingen.

He received his education, first at the Gymnasium, and afterwards at the University of Göttingen, where he was a pupil of Wöhler from 1838 to 1842. At this time a vacant assistantship in Bunsen's laboratory at Marburg offered great attractions for young Kolbe, and here he became practically acquainted with gas analysis, which had just been brought to a high degree of perfection by Bunsen. In the autumn of 1845, he accepted the post of assistant in the organic laboratory of

the Museum of Practical Geology in London, then under the direction of Dr., now Sir Lyon, Playfair, who was at that time engaged in the investigation of gases occurring in coal mines. Before coming to England, Kolbe had already published the results of several highly important investigations; whilst a student at Göttingen, a paper of his appeared on the composition of the fusel oil of grain spirit (1842), and another, in conjunction with Wöhler, on the action of chlorine on carbon bisulphide (1843). The latter reaction was afterwards made the subject of an elaborate research by Kolbe in Marburg, resulting in the discovery of chlorocarbonylsulphuric acid. This research attracted the marked attention of Berzelius, who devoted no less than 10 pages of his Annual Report for 1846 to the discussion of Kolbe's paper. Of still greater interest was the almost simultaneous discovery of trichloroacetic acid amongst the products of the same reaction, and the transformation of this body into acetic acid by the action of potassium amalgam. Kolbe thus contributed to synthetical chemistry the second organic compound built up from its elements without the intervention of organised life, Wöhler having synthesised urea 18 years previously. Before leaving Marburg, he communicated to the Chemical Society a remarkable paper, entitled "Contributions to the Knowledge of Conjugate Compounds," which was printed in the *Memoirs and Proceedings of the Chemical Society*, vol. ii. Kolbe, therefore, came to England with a considerable reputation, and soon after his arrival he communicated to the Chemical Society in rapid succession papers "On the Formation of Nitric Acid in Eudiometric Combustions of Gases Mixed with Nitrogen," "On the Oxidising Power of Oxygen when Disengaged by means of Voltaic Electricity," "On the Decomposition of Valeric Acid by the Voltaic Current," and, in conjunction with Frankland, "On the Chemical Constitution of Metacetic (Propionic) Acid and some other Bodies related to it."

Some of these researches were of a far reaching character, and to them and their subsequent development, chiefly in Kolbe's hands, we owe our present ideas of the constitution of the fatty acids. It is curious to find expressed even in these early papers, the marked views with reference to purely speculative hypotheses which continued to be strongly felt by him to the end of his life. The following words might have been written in one of his last memoirs instead of in one of his first, 40 years ago:—"Those who, leaving the safer road of experiment, plunge into the depths of hypothesis, and build up theories apparently ingenious, frequently stumble and fall amongst a host of contradictions. It is a common error, as experience teaches, into which young chemists are very apt to fall, that, persuaded of the infallibility of their own views, and blind to well-founded objections,

they endeavour to convince by quick and ready argument rather than by solid reasoning, and consequently they either offend others or feel themselves offended when contradicted."

Kolbe returned to Marburg in the spring of 1847, and on his leaving England he was elected a Foreign Member of our Society. In Bunsen's laboratory in Marburg, he prosecuted his researches on the electrolysis of the fatty acids with great success, and in conjunction with Frankland, whom he persuaded to accompany him to Germany, completed during the ensuing summer the study of the saponification of the nitriles, and the action of potassium on ethylic cyanide. In the autumn of the same year, he removed to Brunswick, in order to undertake for Messrs. Vieweg and Son the active editorship of *Liebig and Wöhler's Handwörterbuch der Chemie* and *Otto-Graham's Manual of Chemistry*. This literary work was very onerous, but it gave to chemical literature some of the ablest articles ever written, for Kolbe was a thorough master of his own language, and for clearness, conciseness, and force has rarely been equalled, and never surpassed—an accomplishment which made him somewhat aggressively intolerant of the careless slipshod style of some modern German writers. He held that the German language was being degraded in the scientific journals. His text-books on inorganic and organic chemistry are not only most lucid expositions of our science, but also models of pure and classical German.

In Brunswick he had neither leisure nor opportunity for experimental research, but during his residence there, for upwards of three years, he occasionally visited Marburg for a short time, in order to complete his study of the electrolytic decomposition of the fatty acids, the results of which are embodied in an elaborate monograph published in the second volume of our Journal. He also published several important theoretical papers, as, for instance, "On the Chemical Constitution and Nature of Organic Radicles," published in vols. iii and iv of our Journal, in which, still adhering to the doctrine of conjugate compounds, he ingeniously seeks to reconcile certain objections to the radicle theory by the hypothesis of conjugate radicles. Thus he represents acetyl as carbon in conjugate combination with methyl, and acetic acid as the oxide of this conjugate radicle. The essence of this theory was the assumption of a peculiar kind of chemical combination which did not affect the further combining powers of the element to which the conjunct or copula was attached. Kolbe introduced into notation a peculiar symbol for this kind of combination. Thus he represented acetic acid as oxalic acid conjugated with methyl, $((C_2H_3)C_2O_3.HO)$, and cacodylic acid as arsenious acid conjugated with methyl, $((C_2H_3)_2AsO_3.HO)$. This hypothesis, although finally

rendered untenable by the discovery of the laws of atomicity, was the guiding principle in much of Kolbe's interesting work. It affords a good illustration of the value of even a false theory when it supplies a stimulus to experimental investigation. After the abandonment of the essential principle of the theory of conjugate compounds, Kolbe, in conjunction with Frankland, in 1856 extended the doctrine of atomicity to carbon compounds, and showed the derivation of the fatty acids, aldehydes, ketones, alcohols, and ethers from carbonic anhydride.

Notwithstanding his somewhat vehement antagonism to the modern views of atomic groupings, Kolbe has the strongest claims to be regarded as the author of structural chemistry.

In 1851 he was called to Marburg, to fill the professorial Chair vacated by Bunsen, and was thus enabled once more to resume his experimental work. Besides a number of important papers on theoretical subjects, his work in Marburg included the production of benzaldehyde by the action of nascent hydrogen on benzoyl cyanide, the investigation of the electrolysis of succinic and lactic acids, transformation of lactic acid into alanine (lactamic acid), action of chlorobenzoyl on zincethyl, behaviour of sulphophenylic chloride with hydrogen and zincethyl, transformation of bicarbon acids into monocarbon acids, the introduction of hydrogen into organic compounds, and the synthesis of taurine. The discovery of the diazo-compounds by Peter Griess, then a student with Kolbe, marks an epoch in the history of chemical discovery.

In 1865 Kolbe accepted the invitation of the University to the Chemical Chair at Leipzig. A new laboratory, built under his directions, was opened to students in November, 1868. It was larger and better appointed than any chemical laboratory then existing, and although several of the more modern laboratories surpass it in size and in elaboration of details, the arrangements made by Kolbe were so characteristically simple and complete, that those who have had the opportunity of contrasting it with other similar institutions, especially those who have worked in it, even now consider the Leipzig laboratory to be one of the best of the many magnificent buildings which the wisdom and foresight of our Continental neighbours have placed at the disposal of students of chemistry.

Much important work was carried out under Kolbe's inspiration and direction at Leipzig; the synthesis of oxalic acid from carbonic anhydride and potassium (Drechsel), and that of carbamide from carbonic anhydride and ammonia (Basaroff), two of the most important of the many important discoveries made by Kolbe or his pupils, were both effected before the old laboratory was quitted. The reduction of phthalic chloride; the synthesis of isosuccinic acid; and the

production of nitromethane from chloroacetic acid may also be mentioned. Kolbe appears for years to have endeavoured to obtain nitro-derivatives of acetic acid, and of other non-benzenoid compounds, and was only just anticipated by V. Meyer and Stüber in the discovery of the nitro-paraffins.

Kolbe's greatest achievement during this period, however, having regard to the importance of the discovery to the world at large, was that of the now well-known method of preparing salicylic acid from sodium phenate and carbonic anhydride; that the parahydroxybenzoate is obtained in place of salicylate, when potassium instead of sodium phenate is employed, is one of the most remarkable facts disclosed in this investigation. Arising out of this discovery, we have numerous other important investigations carried out in his laboratory; that of Ost on the formation of polybasic acids from phenols and carbonic anhydride being especially noteworthy.

But Kolbe was not satisfied with the mere discovery of an easy method of preparing salicylic acid; the knowledge that it is very easily resolved into phenol and carbonic anhydride, and that phenol is a powerful antiseptic, led him to think that salicylic acid would be of value as an antiseptic; this was very soon proved to be the case by his own experiments, and by others instituted at his suggestion by medical men. In consequence, salicylic acid is now manufactured in very large quantities; Kolbe, in fact, became the founder of a new industry.

It is difficult at the present day to properly estimate the value of Kolbe's life-work. Of late years the derivatives of benzene and of allied hydrocarbons, owing to their beauty and the ease with which, as a rule, they may be handled, have so engrossed attention, the spirit of order and of relation which Kekulé's genius has infused into this branch of chemistry is so fascinating, that we are apt to overlook the services of those who, like Kolbe, originated the framework upon which it became possible to erect such a superstructure as the benzene theory. It may be doubted whether Kolbe ever really fathomed the depths of modern chemical theory; he could not but be struck, however, by the superficial character of much of the work carried out under its inspiration, and in his hatred of all that was superficial, he often condemned too unsparingly. But those who knew the man, and who are able to read between the lines, must feel that when his words are divested of all personal expressions—which, in the irritation of the moment, a man of his strongly marked individuality could not repress—we have in them the outpourings of a mind whose sole desire was to minister to the true interests of our science; thus read, their importance must sooner or later be recognised, and his warnings will not fail to be of influence.

CHARLES ADOLPHE WURTZ was born at Strasbourg on November 26, 1817. His father, Jean Jacques Wurtz, was the pastor of Wolfsheim, a small village in the neighbourhood of the city, and it was here that Charles Adolphe passed his infancy and early boyhood. In 1826 his father was called to Strasbourg, and the boy was then placed at the Protestant Gymnasium there, where he pursued his studies for eight years. Although diligent, he was not a brilliant pupil, and gave but little promise of becoming distinguished. During this time he acquired a liking for botany, and already began to pursue his chemical studies with ardour, reading with pleasure the somewhat obscure works of the philosopher Oken.

In 1834 he was received "Bachelier ès lettres," and left the gymnasium. As his father was anxious that he should follow the profession of medicine, he was placed with Dr. Schneiter, a friend of the family. This gave him the opportunity of pursuing his favourite study, chemistry, and shortly after he had completed his course in this science he was made assistant to Professor Cailliot, with whom he remained until he quitted Strasbourg.

In 1843 he took his degree as Doctor of Medicine, his thesis being "Essai sur l'albumine et la fibrine," which gained him a medal, and he then went to pass a year at Giessen, where Liebig had his laboratory. It was at this time the close friendship with Hofmann was formed, who was then working in the same laboratory. Shortly after his return from Giessen, in 1844, he quitted Strasbourg and went to Paris, where he was most favourably received—the fame of his researches having already preceded him. He went first to Balard's laboratory at the Faculté des Sciences, where he remained but a short time, and then to Dumas. In 1845 he was appointed Dumas' assistant at the École de Médecine, and in 1849 he delivered the course of lectures on organic chemistry in place of Dumas, who was then busy with political and administrative affairs. His laboratory at this time was dark, gloomy, and inconvenient, and anything but congenial to his neat and orderly habits and cheerful disposition; so being anxious to obtain better accommodation, in 1850 he associated himself with two young chemists, Dollfus and Verdeil, who had just returned from Giessen, and opened a laboratory in the Rue Garancière. Here they worked diligently at chemical research, but unfortunately were soon obliged to move as the house was sold to a printer.

At this time the Institut Agronomique was founded at Versailles, and he was appointed Professor of Chemistry, his friend Verdeil being his assistant. The Institut was suppressed, however, shortly afterwards, and Wurtz lost his chair.

In 1853 Dumas, having resigned his chair at the Faculté de Médecine, and Orfila, who was Professor of Inorganic Chemistry and Toxi-

cology, dying about the same time, the two offices were amalgamated, and Wurtz was appointed. In his new sphere he found a laboratory to his taste—a large room, lofty and well lighted, and capable of containing a dozen workers. Here, and in the temporary laboratory installed during the rebuilding of the *Faculté de Médecine*, most of his work was done, surrounded by many who have since become distinguished in the science, and having with him his old master M. Cailliot, who had been driven from Strasbourg by the German occupation.

In 1874, a chair of organic chemistry was created for him at the Sorbonne, and shortly after he was elected *Maire* of the 7th Arrondissement, the uncongenial duties of which he conscientiously fulfilled, paying especial attention to education. In 1881 he was made a Senator.

His health had always been excellent, but in the winter of 1883–4 he seemed to be somewhat feeble, and went to Cannes, where he saw Dumas for the last time. He had only just returned to Paris when he heard of his friend's death. He was obliged to go to Liege on business, and, in order to pay the last honour to the great chemist, he hurried back. The fatigue was too much for him, and his friends were impressed with the change in his appearance. Notwithstanding, he began his course of lectures, but was unable to complete it, although his state did not seem to be serious, either to his friends or to himself. He died suddenly, and on Monday May 12, 1884, the *Académie des Sciences* learned that the pupil had followed his illustrious master and friend, Dumas.

His work as a chemist and a philosopher is too extensive and too well known to need comment here.

Mr. G. T. ATKINSON was born at Appleby, in Westmoreland, in 1841. He died August 23, 1884. He received his early education at Appleby Grammar School. For some time before he left he was head boy, and according to the custom of the school acted as usher; in this way he gained some experience of teaching. At a comparatively early age, in 1859, he proceeded to Queen's College, Oxford, having gained a Hastings Exhibition. Here, at first, he chiefly studied the classical languages, in which he took a third-class at *Moderations* in 1861. Thereafter his chief attention was given to Natural Science, and he obtained second-class in the Natural Science Schools in 1863. After this he is understood to have worked for some time with the late Professor Rolleston, to whose influence his first interest in natural science is largely to be attributed. Subsequently he engaged in school work, and, about 1869, he became assistant to Dr. Debus, who was then Lecturer in Chemistry at Clifton College. The science of

Clifton in those days, and after, owed much to the good work he did in that and other capacities. After an interval of study in the laboratories at Bonn, Mr. Atkinson returned to Clifton as Assistant Master, in which position he remained to within a few months of his death.

Mr. Atkinson did not write much; but for many years he did earnest work as an abstractor for the Society's Journal, and when at one time, for health's sake, he found it necessary to reduce his labours, although he had considerable private calls upon his resources, he submitted to pecuniary loss rather than cease this work for the furtherance of chemistry.

Dr. ADRIAN BLAIKIE, Sub-Inspector of Alkali Works, at Newcastle, died at the early age of 29 years. He was the son of the Rev. Professor Blaikie, D.D., of the Free Church College, Edinburgh. After receiving his education at the Edinburgh Academy and Fettes College, he went to reside in Stuttgart, when, after studying chemistry with Professor Von Marx for two years, at the Polytechnicum, during the latter portion of which he acted as assistant, he returned to Edinburgh, and entered its University as a student of science and medicine. He successively took the degrees of Bachelor and Doctor of Science, and was awarded the Baxter Physical Science Scholarship, and the Hope Chemistry prize, at that time the two highest honours attainable in his special department; and he completed two years of medical study. During that time he published, along with Professor Crum-Brown, a series of papers on certain organic compounds of sulphur, in the Proceedings and Transactions of the Royal Society of Edinburgh. Owing to ill-health he took a voyage to South America, where he spent six months; and shortly after returning to this country he was appointed Lecturer and Demonstrator at University College, Bristol. At the beginning of 1882, Dr. Blaikie was appointed by the Government to assist the late Dr. Robert Angus Smith in his important duties as Inspector of Alkali Works; and while there, he displayed great skill, industry, and good judgment; and he soon became the trusted friend of his chief. On the death of Dr. Smith, in May of last year, Dr. Blaikie was appointed to the responsible position of Inspector of Alkali Works in the Tyne district, and in August he entered on his duties. But in the last week of November, Dr. Blaikie, who had never been strong, was seized with a return of his old trouble, which manifested itself as intermittent fever; and after a lingering illness, he died at his father's house in Edinburgh, on the 7th February.

In Dr. Blaikie, the Society has lost one who, though young, yet showed promise of great usefulness. It is seldom that such un-

finching perseverance under difficulties, such unswerving integrity, and such practical knowledge are combined with such tact, firmness, and, at the same time, sweetness of disposition. As a demonstrator, he was without an equal in the experience of the writer ; for he made the interests of the students he taught his own, and thereby gained not only their esteem but their friendship. And as he carried this disposition into all his relations of life, there can be no doubt that his orderly and precise character, his power of being firm without giving offence, and his great acquaintance with and ability to handle the problems of industrial chemistry, would have won him a high place in the sphere to which he had devoted his life. By his early death, the Government have lost an able and conscientious servant, and very many a true and valued friend.

Mr. JAMES FORREST, of 12, Langdale Road, Greenwich, was born in 1837. In addition to his analytical practice he had superintended the Guaranteed Manure Companies Works at Millwall for a period of twenty years. He was a devoted scientific worker, and possessed the rare qualities of erudition with humility and firmness of character. He had deep religious feeling and was a warm-hearted man and of a cheerful disposition. He was universally respected. Mr. Forrest was elected a fellow of the Society in 1866. He died on June 27, 1884, aged 47, leaving a widow and four children.

ROBERT HARVEY, M.D., was born in 1833. He received the earlier part of his professional education at the Madras Medical College, subsequently visiting this country, when he qualified as F.R.C.S. Edin., and L.R.C.P. London. On returning to India, he entered the subordinate medical service, in which he attained the rank of honorary surgeon. The record of his services shows that he became assistant to the Professor of Chemistry at the Madras Medical College in 1862, and was subsequently, on three separate occasions, acting chemical examiner to Government, and once acting Professor of Chemistry. For some time previous to his death (which occurred on the 22nd March, 1883), he had been discharging the duties of Professor of Materia Medica, Botany, and Medical Jurisprudence at the local medical college. In the last annual report of that institution it is said that—"By his death the College has lost an experienced teacher who exercised much influence for good over the student." He was elected a Fellow of the Chemical Society in 1881.

Dr. JAMES WILLIAM HUDSON, F.S.A., grandson of Admiral Chas. Hudson, died on June 24, 1884, aged 72. He was educated in Germany, and was author of the "History of Adult Education," and

Founder of the Association of Lancashire and Cheshire Mechanics Institutions, also for ten years secretary of the Manchester Athenæum, having previously held a similar office in Leeds and Glasgow. His life was chiefly devoted to the education of working men and women, encouraging night classes in mechanics' institutions, &c. He was elected a Fellow of the Society in 1867.

FRANCIS MONTGOMERY JENNINGS was born at Cork, where he received his education at the school held by Messrs. Hamblin and Dr. Porter. He was descended from a family who for generations had applied themselves to scientific pursuits, making the study of chemistry a special one; his grandfather having established one of the most successful and extensive mineral-water manufactories in the south of Ireland. Mr. Jennings was fond of extending his inquiries abroad, and used yearly to visit some European capital, thus adding to his extensive field of observation. In 1854, he travelled through North and South America; in 1856 through Spain and Morocco; and, in 1857, through the Holy Land, in company with his brother-in-law, the late Judge Wills, and Sir Henry Holland.

He was a member and frequent contributor to the proceedings of the local societies for the promotion of literature and science in his native city, the Cork Cuvierian and Archæological Society, and the Cork Scientific and Literary Society, of each of which he was one of the founders. He was also a member of the Royal Irish Academy, and took much interest in the work of that body.

He was author of "An Inquiry into the Causes of the Poverty and Discontent in Ireland, with Suggestions for their Removal, Dublin, 1866," and "The Present and Future of Ireland as the Cattle Farm of England, and her probable Population, with Legislative Remedies, Dublin, 1865." He also published some account of "The personal Ornaments, Dress, Arms, &c., of the Inhabitants of Spain and Morocco," as well as of the Holy Land.

Indeed, it would be difficult to meet a mind so well stored with information, calculated at the same time to instruct and delight.

Mr. W. R. JONES, of Pennfield, Wolverhampton, was engineer and manager of the Dewsbury Corporation Gas and Waterworks, Savile Town, a position he held in a very efficient manner. He was elected a Fellow of the Society in 1871, and died on May 9, 1884.

MARK J. LANSDELL was born in 1829 at Battle, Surrey. When but a child he gave early signs of being possessed of a superior intellect. About the age of twenty-two, he entered the laboratory of the late John Nisbet, analytical chemist; he studied with the intention of

becoming a brewer, but being dissuaded from this he remained as assistant with his teacher. In 1863 he entered into partnership in the business of the late Mr. Nisbet, who died in 1882, the firm taking the name of Nisbet and Lansdell. In 1881 he retired, and afterwards resided at Hastings, where he died on October 12, 1884.

Mr. Lansdell was a man of unobtrusive and retiring habits. He took much interest in the progress of science, and was possessed of a mind stored with a great amount of information. He was elected a member of the Chemical Society in 1859.

JAMES NAPIER was born in 1810, at Partick, near Glasgow, and received the earlier portion of his education in a small day school in that suburb. Owing to the straightened circumstances of his parents, he was taken from school at an early age, and began work in calico-printing works in the district. At the age of twelve or thirteen, he was placed in his father's trade—that of a hand-loom weaver; but being desirous of more education he set to work to earn money for this end, and made himself proficient in writing and arithmetic.

Owing to the dulness in the weaving trade, Napier betook himself to that of a dyer, finding employment in the works of Messrs. Gilchrist, Partick, where, after two years' service, he became foreman.

Shortly after 1833 he fell into a feeble state of health, and having been advised by his medical man to leave the dyeing trade he did so, and devoted himself to establishing a lending library. This, however, did not succeed, and he ultimately returned to the works of Messrs. Gilchrist. Prior to this he had published an essay on "Dyeing," which brought him into the notice of Mr. J. J. Griffin, who had then a publishing business in Glasgow, to which was added that of a dealer in chemicals and philosophical apparatus. Mr. Napier was taken into their employment as an assistant, and it was doubtless at this time that he first became acquainted with the late Dr. James Young, F.R.S., then assistant to the late Professor Graham, this early acquaintance leading to a continued friendly intimacy.

In the year 1839 he was employed by Mr. J. J. Griffin to carry out some experiments on electrotyping, and these experiments brought him under the notice of Messrs. Elkington, to whose electroplating works in London he removed in 1842; in a short time he obtained full charge of both the plating and gilding establishments.

There being few manuals at that date written on such processes, many persons consulted Mr. Napier on the application of electro-deposition to their particular industrial requirements; and in consequence of such a request from the Parys Mines in Anglesea, he commenced a series of experiments on the application of electricity to the extraction of copper from the ore when in a state of fusion. Acting

on the advice of Mr. Smith, then an influential member of Messrs. Elkington's firm in London, he took out patents for his processes, and went first to Swansea and then to Holywell, in Flintshire, to try the process on a large scale. The success ultimately attending the carrying out of these experiments was much diminished by the worst features of the Trades' Union of those days, and Mr. Napier having parted with the rights of the patent in full to Mr. Smith, all profits vanished on the death of the latter gentleman, whose affairs were left in a state of bankruptcy.

In the year 1852, Mr. Napier revised and extended his magazine articles, and published, through Messrs. Griffin, "A Manual of the Art of Dyeing," and later, in 1857, through the same publishers, he brought out "A Manual on Electro-metallurgy, including the applications of the Art to Manufacturing Processes."

Mr. Napier returned to the neighbourhood of Glasgow in 1849, where most of his literary work was done, and where he took a great interest in the sanitary conditions and movements then being made in his native place. In 1860, at the request of Lord Breadalbane, he was asked to visit and inspect a copper mine at Killin, on the south side of Loch Tay, where it was thought there might be some probability of a profitable working. The quality of the ore, however, from the mine deteriorating, the scheme was ultimately abandoned. In 1861, Mr. Napier returned to Glasgow, where he commenced business as a consulting chemist, and erected also some small oil of vitriol works. Being relieved to a considerable extent from the duties of management by his eldest son, he returned to his literary pursuits, and published some books chiefly of an antiquarian nature.

Mr. Napier was a Fellow of the Royal Society of Edinburgh, of the Chemical Society, and member of the Natural History and Archæological Societies of Glasgow; and on several occasions a member of the Council of the Philosophical Society. He was the author of twenty-eight papers, besides several other shorter communications to various journals.

Mr. Napier died on December 1, 1884, at the age of seventy-four.

Mr. J. L. SHUTER died at his residence, Steel Road, Haverstock Hill, on December 16, 1884, in the sixty-fifth year of his age.

He had been settled in the city of London about thirty years, and served in various public capacities. His name was prominently before the public some years back in connection with what was known as the "Peter Daly" case, his action leading to an entire change in the medical régime in relation to the sick poor. Mr. Shuter always took great interest in scientific matters, and became a Fellow of our Society in 1872.

Though debarred from directly furthering the advancement of science by the nature of his pursuits, Mr. Shuter was a man who can ill be spared, for he brought into practical public life a spirit appreciative of the value of scientific research. If that consummation, devoutly to be wished—the general application of truly scientific principles to the arts, manufactures, and agriculture—is ever to be attained, it must be through the aid of such men as J. L. Shuter.

THOMAS KING ROGERS was born in 1850. He received his professional education at University College, London, and graduated as M.B. at London University. He was also a F.R.C.S. and L.R.C.P. of London, and a Fellow of the Institute of Chemistry. He joined the Indian Medical Service in 1877, and arrived in Madras in the same year. He was employed on medical duty till July, 1879, when, on the appointment of Chemical Examiner to Government and Professor of Chemistry at the Medical College falling vacant, he was nominated to it, and continued to discharge the duties of the office until his death from typhoid fever on the 12th June, 1884. He became a Fellow of the Madras University in 1881, and for a few months prior to his death held the post of Lecturer on Chemistry at the Madras Agricultural College. He is alluded to in the last Annual Report of the Medical College in the following terms: "The late Prof. T. K. Rogers * * * was an able and successful teacher, and enthusiastically devoted to his work. His loss is deeply regretted by his colleagues and by the students, with whom he was very popular." He was elected a Fellow of the Chemical Society in 1881.

ROBERT ANGUS SMITH was born near Glasgow in 1817. After passing through the High School of that city he was sent to the University, where he quickly showed that liking for the classics, and especially for Greek, which clung to him through life, and his mother, as usual among Scottish matrons, cherished the aspiration that her son should "wag is pow in a poopit." Whether this ambition was at any time shared by her son is doubtful; at all events such a career became impossible for Smith after hearing the preaching of Campbell of Row; he declared that he could not take "holy orders in a kirk which had expelled a man for being apparently both better and wiser than itself." On leaving the University, he acted as tutor in various families in the Highlands and in London. Whilst at the University his leaning towards science had manifested itself, and in company with his brother John, who is known as the inventor of a chromoscope and as the author of some speculations on the cause of colour and the nature of light, he read the standard works of his time on natural philosophy and chemistry. At 22 he went to Giessen, and

after working under Liebig for some time he obtained his doctorate, returning to England in 1841, when he procured employment under Dr., now Sir Lyon, Playfair, in connexion with the Health of Towns Commission. It was this circumstance which doubtless served to fix the direction of much of his future work. His earliest communication to our Society was on the air and water of towns, and successive memoirs with almost identical titles made their appearance either in our Transactions or among the Reports of the British Association. The Royal Society's Catalogue shows that Smith was the author of about thirty papers on air and rain. These he eventually collected and published with considerable additions, in the form of a thick 8vo. volume, entitled "Air and Rain, the Beginnings of a Chemical Climatology," with a dedication to his friend and teacher Liebig. Smith's literary skill and critical faculty are, however, seen to better advantage in the short memoir on Graham prefixed to the collection of that philosopher's papers brought together and published, with a reverential care, by the late Dr. James Young. Smith had years before saturated his mind with the notions of the Hellenic atomists, even before the time he wrote his monograph on Dalton, and in this short prefatory memoir of some twenty pages he crystallises out his thoughts on the development of the atomic systems of Kapila, Leucippus, Lucretius, Newton, and Dalton, and shows with admirable lucidity Graham's true relation to these great thinkers.

From 1842, Angus Smith was closely connected with Manchester. In that year he settled himself in the town as a consulting chemist. Shortly afterwards he became a member of the Literary and Philosophical Society of Manchester—a society made famous by its connection with Dalton and the Henrys—and much of his work appears in the memoirs and proceedings of that body. In his "Centenary of Science in Manchester," published a short time ago, he has sketched, in characteristic manner, the growth of that institution, and has sought to trace its influence on the development of scientific life in Lancashire.

In 1863 Angus Smith was appointed Inspector-General of Alkali Works by the Government, and the somewhat delicate task of initiating the working of Lord Derby's Act fell to him. He performed this duty with characteristic tact, and with every desire to avoid undue interference with the legitimate business of the alkali maker. The successful working of that Act is largely due to the manner in which Angus Smith and his subordinates set it in operation. On the passing of the Rivers Pollution Act, he was made Inspector for England, and afterwards for Scotland, and he held these appointments up to the time of his death.

Angus Smith became a member of the Chemical Society in 1845, and

a Fellow of the Royal Society in 1857: in 1882 the University of Edinburgh conferred upon him the honorary degree of LL.D.

SIDNEY GILCHRIST THOMAS was born in April 1850, and was educated chiefly at Dulwich College, with a view of entering the medical profession, in which his brother, Dr. Llewellyn Thomas, was a well-known specialist, although his own inclinations were towards engineering. His father's death, however, rendered this impossible, and at the age of seventeen he entered the Civil Service. His predilections, however, lay in a scientific direction, chemistry and metallurgy being his especial favourites. Engaged during the day, his only opportunities of study were in the evenings. A small laboratory at home was the scene of much of his study, in which he obtained further guidance by attendance at the laboratories of Mr. Arthur Vacher, of Great Marlborough Street, and of Mr. George Chaloner, of the Birkbeck Institution.

It was in 1870, while attending a course of lectures on metallurgy at the Birkbeck Institution, that the idea of dephosphorisation first took strong hold upon his mind. He proceeded in a strictly logical manner in the study of his chosen subject. Collecting all the data, both chemical and practical, he came to the conclusion, as Gruner had done, that the acid lining of the converter was the great enemy to dephosphorisation, and from this to the idea of a basic lining was a natural step. True, a lime lining had been used in puddling furnaces even before 1850, but the difficulty always had been to make it stand. Numerous experiments appeared to show that a small admixture of silicate of soda with lime, or magnesian lime, or Portland or Roman cement, would give good results, and about 1876 Thomas obtained the able assistance of his cousin, Percy C. Gilchrist, who was then chemist at the Cwm-Avon works, but soon after went to Blaenavon, where an immense number of experiments were tried. Thomas systematically theorised and planned experiments, keeping up a continual correspondence with his cousin, who carried them out, besides working independently and conferring with him. In November, 1877, Thomas took out his first patent; but events moved with him so quickly that in a letter dated July 2, 1878, he says, "I regard it as somewhat out of date," and, as a matter of fact, patent succeeded patent up to the present year.

Matters up to this time had of course been kept very secret. He had but two or three confidants, but the need for experiments on a larger scale led him to seek the aid of Mr. Martin, the manager of Blaenavon, who enabled the experimenters to work with converters holding as much as half a ton, while at Dowlais, through the courtesy of Mr. Menelaus, a few blows were made with a 5-ton converter. On

March 28, 1878, the first public announcement was made to the Iron and Steel Institute by Mr. Sidney Thomas, in the discussion on Mr. I. Lowthian Bell's paper on the separation of phosphorus from pig-iron in a furnace lined with oxide of iron. Thomas' paper, describing details of the process, was down for reading at the Paris meeting of the Institute in September, 1878, but was last on the list, and was needlessly postponed until the following May, when it was discussed with the greatest interest by a crowded meeting. Copies of the paper had been liberally distributed in Paris, and had been carried thence all over Europe and America, so that every one interested had had six months to study and criticise it.

Meanwhile Mr. Windsor Richards, of Bolckow, Vaughan, & Co., was prevailed upon to try the process. This he did with the greatest thoroughness and fairness, and ultimately adopted it in the works under his management. From this also much of the foreign appreciation of the process is certainly due, owing to the facilities given by Mr. Richards for study by visitors. A claim to priority had been advanced by Mr. Snelus, and a contribution towards basic brick-making had been made by Mr. E. Riley, both of which were met with characteristic fairness by Thomas, and, instead of going to law between themselves, the parties accepted the arbitration of Sir William Thomson as to their respective shares in the ownership of the amalgamated patents. It should be mentioned in this place that, although several persons worked at basic processes before Thomas, not a ton of metal was made by such processes before 1878. Thomas' foreign patents proved a source of great profit, while in England but a comparatively small return has been made.

All the delicate task of negotiating the sale of patents and contesting their validity abroad fell to the share of Thomas. German manufacturers who appropriated without payment the inventions of Bessemer and Siemens, attempted to do likewise with Thomas, but he beat them on their own ground, and successfully argued the case personally at Berlin before a court specially constituted. The exertion of constantly travelling, combined with the anxiety of perpetual work, ultimately, however, ruined Thomas' health, which was never very robust. In 1882 he was ordered to pass the winter in Australia, whither he went *viâ* India, and returned through the United States. On this journey, however, he did much work, and came back in the early summer as full of ideas as ever. He only stayed in England a few months, and in September left again for Algeria, tended by an affectionate mother and sister, who had broken up their home to solace his exile. At Bir el Droadj he set up his habitation, including a laboratory, and worked away at the utilisation of phosphoratic slag and other problems. Last summer he moved

north to Paris, where he submitted himself to a method of treatment which promised good results, but the improvement was only apparent, and he died on the morning of Sunday, February 1, 1885.

JOHN CHRISTOPHER AUGUSTUS VOELCKER, was born on September 24th, 1822, at Frankfort-on-the-Maine. He was the fifth son of Frederick Adolphus Voelcker, a merchant of that city, who died when Augustus was only eleven years old. During his boyhood, Augustus suffered from very delicate health, which greatly retarded his early education. This he obtained at a private school in the town. About the age of 22 he went to the University of Göttingen, chiefly for the purpose of studying chemistry under Wöhler. Here he took the degree of Doctor of Philosophy in 1846, the subject of his inaugural dissertation being the composition of tortoise-shell. From Göttingen he paid a short visit to Giessen, where Liebig had established a school of chemistry. Liebig had, at that time, for some years paid special attention to the applications of chemistry to agriculture, and had already published his two memorable works on that subject.

Whilst at Göttingen, Voelcker published four papers on the compounds of manganese, and of some other metals. At this time a paper of his on the occurrence of mannite in the roots of *Triticum repens* appeared; and also one on the analysis of poppy-oil.

It was also whilst he was still at Göttingen, that Mulder paid a visit to Wöhler at that place, and, on Wöhler's recommendation, engaged Voelcker as his principal assistant; he accordingly returned with him to Utrecht, where he remained for some time. Dr. Voelcker assisted Mulder in his various investigations, and it was doubtless to this work that his devotion to agricultural chemistry owed its origin and its stimulus.

During Voelcker's stay at Utrecht, Professor J. F. W. Johnston, of Edinburgh, who was Chemist to the Agricultural Chemistry Association of Scotland, paid a visit to Mulder, and induced Voelcker to go to Edinburgh to take charge of the laboratory of that Association. He went to Edinburgh in February, 1847, and remained there until August, 1849; with the exception that he spent from November, 1848, to February, 1849, at Durham, at the University of which place Johnston was Professor of Chemistry, and for whom he lectured, and worked in the Laboratory, there.

At Edinburgh the whole of the responsibility, both as analyst and consulting chemist, frequently devolved upon him, Professor Johnston spending much of his time at Durham, or being otherwise engaged. It was under these circumstances, that he first gained experience in the requirements of practical agriculture; being constantly in communication with practical farmers, and investigating

and advising on the problems they brought before him for his solution; this contributed in no small degree to his success as a teacher, a scientific adviser to the practical farmer, and in his profession as a consulting chemist generally.

During his stay in Edinburgh, he made the acquaintance of the late Professor George Wilson, in whose private laboratory he worked for a short time. In August, 1849, he left Edinburgh, being appointed Professor of Chemistry at the Royal Agricultural College, Cirencester; and from this time he began a still more active life of lecturing, writing, and experimenting. His income at the College was small, but he supplemented it by writing and by analytical work.

It was about this time, or soon after, that he contributed papers on various subjects of investigation to some Scotch Scientific and Agricultural Journals.

In 1842 Dr. Voelcker went to Frankfort to be married, and he returned to Cirencester with his wife. Mrs. Voelcker, four sons and one daughter, survive to mourn his loss. His eldest son, George, died in 1876, at the age of 23, after having prosecuted his studies in medicine with great industry and success, and nearly completed his course with apparently a career of much promise before him. He had contracted diphtheria in the discharge of his hospital duties, and died after a very short illness. His loss under these painful circumstances was always most keenly felt by his father.

In 1855 Dr. Voelcher was appointed Consulting Chemist to the Bath and West of England Agricultural Society; and he held the office up to the time of his death, a period of nearly thirty years. In this capacity he gave lectures at various places from time to time, instituted field and other experiments, conducted much laboratory investigation, and contributed papers to the "Journal" of the Society.

In 1852 his first paper in the "Journal of the Royal Agricultural Society of England" appeared. He also contributed one in 1855, one in 1856, and one in 1857. In that year, 1857, he was appointed Consulting Chemist to the Society; and from that time to the date of his death, about twenty-seven years, he contributed one or more papers to every half-yearly number of that Journal.

For about six years after his appointment as Consulting Chemist to the Society, he still retained his Professorship at Cirencester; and he availed himself of the opportunities which the College farm afforded, for carrying out various experiments at the homestead, and in the field, which were supplemented by collateral laboratory investigations. In his reports of field experiments, he conscientiously recorded failures as well as successes, and he was very careful not to draw general conclusions from results obtained on land of one de-

scription, in a given condition from previous treatment, or in one season only. He hailed with much satisfaction the inauguration of the more systematic series of field experiments now in progress at Woburn, conducted there on behalf of the Royal Agricultural Society, at the instance, and at the cost, of His Grace the Duke of Bedford. These experiments were commenced in 1877. In the following year the conduct of them devolved entirely upon Dr. Voelcker himself, and to the day of his death he took the deepest interest in their management, and in their results.

Very soon after he had devoted himself to Agricultural Chemistry, Dr. Voelcker commenced to pay attention to the various aspects of the subject of the Feeding of Animals. He had not the same facilities, either for conducting feeding experiments himself or for arranging with others to conduct them, that he had in case of field experiments with manures. He, however, not only wrote and lectured on the chemistry of the feeding process, but he analysed a very large number of food-stuffs, both home-grown and imported. But perhaps the most essential service he rendered to farmers generally, in connection with the value of food-stuffs, was by his elaborate investigations, microscopic and chemical, of the various matters entering into the composition of feeding-cakes, by his numerous analyses of them, and by his fearless and persistent exposure of what he considered to be injurious in the manufacture or composition of such articles, whether resulting from carelessness, ignorance, or fraud.

The subject of *Milk* and the *Dairy*, which is one of rapidly growing importance to the British farmer, was early taken up by Dr. Voelcker. In connection with it, he has executed a great amount of analytical work, made many experiments in dairy management, given several lectures, and published not a few papers recording existing knowledge, and the numerous results of his own investigations.

In addition to numerous articles in the *Journal of the Royal Agricultural Society*, Dr. Voelcker from time to time contributed papers to our Society, and in some cases he gave the same results in less technical form in the *Journal of the Royal Agricultural Society*. Of those communicated to both Journals, the one involving by far the largest amount of laboratory investigation, and leading to the most important conclusions, both practical and scientific, related to the composition of the waters of land-drainage, and to the loss of plant-food thereby. In the earlier years Dr. Voelcker also frequently contributed papers at the meetings of the British Association for the Advancement of Science.

He was elected a member of the Chemical Society in 1849; was several times a member of the Council of the Society; and was one of its Vice-Presidents at the time of his death. He was elected a Fellow

of the Royal Society in 1870. He was one of the founders, and one of the first Vice-Presidents of the Institute of Chemistry of Great Britain and Ireland.

As is well known, on coming to London in 1863, in addition to his duties as Consulting Chemist to the Royal Agricultural Society, Dr. Voelcker commenced private practice as consulting chemist generally, and established the laboratory in Salisbury Square, which is still carried on by two of his sons, who were his partners before his death. He very soon had an extensive practice, not only in connection with agriculture, but with many other industries, and he was often engaged on important trials. In addition to such cases, he was frequently called upon to give evidence before Parliamentary Committees, or Royal Commissions, in relation to such matters as Gas, Water, and Sewage Bills, the Agricultural Holdings Act, River Pollution, and so on. He was one of the Jurors of the International Exhibition of 1862, of the Fisheries Exhibition in 1883, and of the Health Exhibition in 1884.

There can be little doubt that Dr. Voelcker's life was shortened by overwork. On Sunday, December 23, 1883, he had a not severe attack of paralysis, but it was such as to indicate that absolute rest was essential for some considerable time. As soon, however, as he felt some returning strength, it was impossible to restrain him from returning more or less to his active duties. He had no return of paralysis, but in August, 1884, symptoms of heart disease, with other complications, supervened. From this time he never really rallied, and he died on the morning of December 5th, 1884, at the age of 62. For some weeks he had suffered intensely. His mind was, however, perfectly clear; he fully recognised his position, and was entirely resigned to it. He passed away quite quietly, and without any pain towards the end.

(Autobiography of Henry Watts).

HENRY WATTS was born in London on the 20th of January, 1815. After receiving the usual school education in classics and mathematics, with the addition—unusual at that time—of good elementary instruction in Physics and Chemistry, he was articled at the age of fifteen to an Architect and Surveyor; but finding, after a few years, that he had entered a profession for which he was by no means adapted, he left it, and employed himself for some years in teaching—chiefly mathematical—partly as a school assistant, partly as a private tutor. In 1841 he graduated, as Bachelor of Arts, in the University of London. In 1846 he entered the Birkbeck Laboratory of Chemistry, then recently established at University College, as assistant to his highly valued friend, the late Professor Fownes, and in that capacity was engaged

in directing the work of the students till the death of Professor Fownes in 1849, and afterwards till 1857 under Professor Williamson. A Professorship he was unable to obtain, being incapacitated from lecturing by a serious and incurable impediment of speech with which he had been troubled from very early years; and for this reason he was ultimately induced to devote himself entirely to the literature of Chemistry.

In 1848 he was engaged by the Cavendish Society to prepare a translation, with additions, of the great *Handbuch der Chem.* of Leopold Gmelin, a work which extended to 18 volumes, and occupied a large portion of his time for more than 20 years, the last volume and the index having been published in 1872.

In 1858 he was engaged by the eminent publishers, Messrs. Longman and Co., to prepare a new edition of *Ure's Dictionary of Chemistry and Mineralogy*, but finding that this book, the last edition of which appeared in 1831, had fallen too much behind the existing state of Chemistry to be made the ground work of a dictionary adapted to the requirements of the time, he undertook, with the consent of the publishers, and the assistance of a staff of contributors, distinguished for their attainments in different branches of Physics and Chemistry, the compilation of a new *Dictionary of Chemistry and the Allied Branches of other Sciences*. This work, in five large octavo volumes, was completed in 1868, but as additions were required to keep it abreast of the continual advances of science, a supplementary volume was published in 1872, a second supplement in 1875, and a third (in two parts) in 1879 and 1881.

Mr. Watts also brought out three editions of *Fownes's Manual of Chemistry*, viz., the tenth published in 1868, the eleventh in 1872, and the twelfth in 1877.

He held for many years the appointments of Editor of the *Journal* and Librarian to the Chemical Society, having been appointed to the former in 1850 and to the latter in 1861. He was elected a Fellow of the Chemical Society in 1847, a Fellow of the Royal Society in 1866, and a Member of the Physical Society in 1879. He was also an Honorary Member of the Pharmaceutical Society, and a Life Governor of University College, London.

He was married in 1854 to Sophie, second daughter of M. Henri Hanhart, of Mulhouse in Alsace, and became the father of a family of eight sons and two daughters.

This short autobiographical sketch was found after Mr. Watts's death in his own handwriting amongst his papers and without date. It contains perhaps all that he believed would be of general interest, but some further particulars may be added which will be

welcome to the Fellows of the Society with whom he was connected for so many years.

As a young man he was full of vitality, energy, and enterprise. He had a passionate love of knowledge and rare skill and patience in communicating it. He was an excellent mathematician, a good classical scholar, and he had, what at that time was a rare accomplishment, a knowledge of French and German, to which he afterwards added Italian and Swedish. He was a good scientific botanist, and to these literary and scientific accomplishments he added a knowledge of the fine arts by no means superficial; always an excellent draughtsman, he afterwards attained considerable skill in sketching in water colours.

His knowledge of Chemical literature was probably more extensive than that of any other Englishman, and his skill as an author and editor is too well known to need comment.

At the time of his death he had entered into arrangements for producing a new edition of the *Dictionary of Chemistry*, and was also, in conjunction with Mr. Charles E. Groves, editing a new and enlarged edition of *Knapp's Technology*.

He died very suddenly on the 30th of June, 1884, of syncope arising from failure of the heart's action.

His pleasant manner and invariable kindness, coming as it did from innate good-heartedness, endeared him to all who had the pleasure of his acquaintance.

Accomplished, industrious, good-hearted, his death will long be deplored not only by his many friends, but by all who in this country make Chemistry a pursuit.

GEORGE WILLIAM WIGNER was born at King's Lynn, Norfolk, October 19, 1842.

He was educated at the Lynn Grammar School, and, as a boy, he showed much interest in scientific pursuits. He studied chemistry, electricity, astronomy, and photography, obtaining considerable practical knowledge in these branches of science from private work at home; his friends observing the strong bent of his inclinations assisted and encouraged him in the pursuit of chemistry.

At the age of seventeen he came to London, and shortly afterwards entered as a clerk in a private banking firm, where he remained for some five years, employing his evenings and leisure in the study of chemistry, &c. At this time he commenced lecturing for various schools and societies on chemistry and scientific subjects. It was at the conclusion of one of these lectures he made the acquaintance of Mr. Frank Hills, of Deptford, and this gentleman offered him a post in the laboratory of his chemical works; here he remained about four

years, and during the latter part of this time he took out several patents for the treatment of sewage; this led to his connection with the Native Guano Company. In 1872 he commenced business on his own account in Great Tower Street, where, by his close attention to business, his sound general knowledge, keen judgment, and ready appreciation of difficult scientific questions, he soon obtained a very large practice, not only with merchants and brokers, but also with chemical manufacturers who sought his advice on new processes, patents, &c. He took a most active part in the Sale of Food and Drugs' Act, and was one of the founders, if not the father, of the Society of Public Analysts, into which he threw his whole energy, acting for many years as honorary secretary, and only relinquishing the post when he was made President in 1883, at the same time editing the *Analyst*, in which the proceedings of the Society are published, and which contains some fifty original papers by him chiefly relating to food and drugs, and their examination.

In 1880, the National Board of Trade of the United States awarded him the first prize of 500 dols. for the best essay and draft Act to prevent injurious adulteration of food and drugs, and to regulate the sale of the same, without imposing unnecessary burdens on commerce.

He was among the first public analysts elected, and acted for three of the largest districts in the Metropolis—Plumstead, Greenwich, and Deptford—and was consulting chemist to many well-known firms, as well as to the Board of the Thames Conservancy: in these capacities he was frequently called into the witness-box, and well known as a shrewd and clever scientific witness.

He acted as judge not only at the various Food Exhibitions, but was one of the jurors at the International Health Exhibition, South Kensington, 1884, when he undertook some hundreds of analyses of the food samples there exhibited.

He lost his wife in January, 1884, and from that time his health gradually gave way, when, after a few weeks of intense suffering, he died from stricture of the œsophagus on October 17, 1884, leaving two children—a boy and girl—in early years.

His life was one of incessant hard work, allowing but little time for the necessary relaxation to maintain health. An active brain stimulating the strongest desires for chemical knowledge lost him to science at the early age of forty-two.

It was then moved by Dr. GLADSTONE, and seconded by Sir F. A. ABEL, that the best thanks of the meeting be given to the President for his address, and that he be requested to allow it to be printed.

This resolution was unanimously accepted, and the President returned his thanks.

Dr. RUSSELL, the Treasurer, then read his report :—The income of the Society for the year was about £3,569, the expenditure £3,283, leaving a balance of only £286; about £2,198 had been expended on account of the Journal, and about £440 on account of the Library.

Mr. MOND proposed, and Mr. MAKINS seconded, a vote of thanks to the Treasurer, to which Dr. RUSSELL replied.

Mr. FRISWELL proposed, and Mr. G. S. JOHNSON seconded, a vote of thanks to the Auditors, Mr. Makins, Mr. R. H. Davies, and Dr. P. F. Frankland. Mr. MAKINS replied.

A vote of thanks to the Officers and Council was then proposed by Mr. WARINGTON, seconded by Mr. RILEY, and replied to by Dr. ARMSTRONG.

Mr. TYRER proposed, and Dr. JAPP seconded, a vote of thanks to the Editor, Sub-Editor, Abstractors, and Librarian. Mr. GREENAWAY replied.

Dr. Plympton and Mr. E. W. Voelcker were appointed scrutineers, and a Ballot having being held, the following were declared elected as Officers and Council for the ensuing year :—

President.—Dr. Hugo Müller.

Vice-Presidents who have Filled the Office of President.—Sir F. Abel, Dr. Warren De la Rue, Prof. Frankland, Dr. J. H. Gilbert, Dr. J. H. Gladstone, Dr. A. W. Hofmann, Prof. Odling, Dr. W. H. Perkin, Sir Lyon Playfair, Sir Henry Roscoe, and Prof. A. W. Williamson.

Vice-Presidents.—Mr. W. Crookes, Prof. G. D. Liveing, Dr. Schunck, Prof. T. E. Thorpe, Dr. Tilden, and Mr. Walter Weldon.

Secretaries.—Dr. H. E. Armstrong and Mr. John M. Thomson.

Foreign Secretary.—Dr. F. R. Japp.

Treasurer.—Dr. W. J. Russell.

Ordinary Members of Council.—Dr. E. Atkinson, Mr. H. T. Brown, Dr. Carnelley, Mr. Carteighe, Dr. F. Clowes, Mr. A. E. Fletcher, Prof. G. C. Forster, Mr. Friswell, Mr. Meldola, Dr. Messel, Mr. Ludwig Mond, and Mr. C. O'Sullivan.

CR.

CR.

THE TREASURER IN ACCOUNT WITH THE CHEMICAL SOCIETY FROM MARCH 24, 1884, TO MARCH 23, 1885.

DB.

		£ s. d.		£ s. d.		£ s. d.		£ s. d.	
Balance at Bank March 24th, 1884		1,704	2 11			312	10 0		
" " in hands of Treasurer			11 8				8 12 4		
<i>Receipts by Admission Fees, Subscriptions, and Life Compositions, from March 24th, 1884, to March 23rd, 1885.</i>				1,704	14 7	100	0 0		
21 Life Compositions		420	0 0			326	3 10		
105 Admission Fees		420	0 0			36	1 9		
1 Subscription for 1881		32	0 0			1,181	1 9		
20 " " 1882		123	0 0			224	4 8		
20 " " 1883		493	0 6					2,198	14 4
202 " " 1884		1,316	0 0						
677 " " 1885									
<i>Receipts by Journal and Index</i>				2,918	0 6				
Subscriptions for Proceedings of Royal Society		310	5 10			37	10 0		
" " from Institute of Chemistry		41	0 0			62	0 0		
" " from Society of Public Analysts		6	0 0			236	9 2		
" " from Crystallographic Society		8	8 0			75	17 2		
Sale of Books		4	4 0			23	12 3		
<i>Dividend on Consols</i>								440	8 7
" Metropolitan Board of Works 3½ per Cent. Stock		117	0 0					33	19 6
" London and North Western Railway Debenture Stock		130	15 11					62	13 0
		30	15 2					16	10 0
								50	6 6
								30	0 0
								8	1 3
								40	8 9
								20	4 6
								27	0 0
								5	5 0
								145	18 0
								5	14 3
<i>Assets.</i>				278	11 1				
Balance at Bank						24	18 0		
" " in hands of Treasurer						18	10 0		
Three per Cent. Consols						49	6 7		
London and North Western Railway Debenture Stock						20	0 0		
Metropolitan Board of Works 3½ per Cent. Stock						52	0 0		
						7	18 0		
						22	1 0		
						2	2 0		
196		15	7						
1		14	11						
770		0	0			1,218	8 0		
1,220		1 4				1	13 4		
5,273		14 6							
<i>Expenses on Account of Journal.</i>									
Salary of the Editor									
Incidental Expenses of Editor									
Salary of the Sub-Editor									
Fees to Abstractors									
Periodicals for Abstractors									
Printing of Journal									
Distribution of Journal									
<i>Expenses on Account of Library.</i>									
Salary of Librarian									
Library Attendant									
Books and Periodicals									
Binding Books									
Expenses for new Catalogue, &c.									
Printing Authors' Copies									
Proceedings of Royal Society, and Distributing same									
Reports of Meetings									
Miscellaneous Printing									
Insurance of Furniture and Books for 7 years									
Inhabited House Duty and Income-tax									
Stationery, Postage, &c.									
Photographs of Presidents									
New Carpets and Oilcloths									
Fee for Medical Attendance on Mr. Hall									
Collector's Commission on Subscriptions									
Treasurer's Stamps and Clerical Aid and Drafts									
<i>House Expenses.</i>									
Providing Refreshments									
Heating the Building									
Lighting									
Cleaning									
Wages of House Porter									
Petty House Expenses									
Repairs									
Gratuity to Gate Porter									
Treasurer's Petty Cash Disbursements									
Purchase of £700 Metropolitan Board of Works 3½ per cent. Stock									
Balance at Bank									
" " in hands of Treasurer									
Audited and found correct. { GEORGE H. MARINE. PEECY F. FRANKLAND. ROBERT H. DAVIES.									
March 25th, 1885.									

THE TREASURER OF THE CHEMICAL SOCIETY IN ACCOUNT WITH THE RESEARCH FUND.
FROM MARCH 24TH, 1884, TO MARCH 23RD, 1885.

Dr.

Cr.

	£	s.	d.	1884.		£	s.	d.
Balance at Bank, March 24th, 1884	336	3	3	Mar. 31. Honorarium to Longstaff Medallist		20	0	0
Subscriptions and donations	115	0	0	June. Purchase of £200 Metropolitan Board of Works 3½ per cent. Stock		218	15	0
Dividend on North British Railway Stock	39	3	4	July. Grants made		75	0	0
" Metropolitan Board of Works 3½ per cent. Stock	123	2	3	1885.				
				February. Grants made		90	0	0
				March 24. Balance at Bank		209	13	10
						<u>£613</u>	<u>8</u>	<u>10</u>
<i>Assets.</i>								
North British Railway 4 per cent. Stock ..	1,000	0	0	Audited and found correct, March 25th, 1885. ROBERT H. DAVIES. PERCY F. FRANKLAND. GEORGE H. MAKINS.				
Metropolitan Board of Works 3½ per cent. Stock	3,700	0	0					
Balance at Bank	209	13	10					
	<u>£4,909</u>	<u>13</u>	<u>10</u>					

XXXV.—*Combustion in Dried Gases.*

By H. BRERETON BAKER, B.A., Brackenbury Scholar of Balliol College, Oxford.

THE recent experiments of Mr. Harold B. Dixon, on the union of dry carbon monoxide and oxygen (*Phil. Trans.*, 1884, Part II), showing that a mixture of these gases does not explode when a spark is passed through them, led me to investigate the question whether moisture is necessary for the combustion of elementary substances in oxygen. Phosphorus and carbon were selected for the first experiments; they were purified in the following manner:—

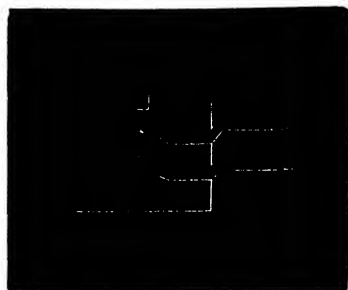
Commercial amorphous phosphorus was washed with water and dried at 100° in a current of carbonic anhydride, previously passed through two wash-bottles of sulphuric acid. One end of the tube containing the phosphorus was sealed, and the other attached to a Sprengel pump. When the air had been removed, the tube was heated in an air-bath at 150—160°. It was thought that occluded hydrogen would be got rid of in this way.

Finely powdered charcoal was heated to a bright red heat in a current of dried chlorine for three hours. The combustion-tube in which this was done was then transferred to an air-bath, and heated at 200°, whilst a current of air was passed through it. The air was dried by passing it through three long nearly horizontal drying tubes, containing sulphuric acid.

Portions of these purified substances (0·5—1 gram) were placed in hard glass tubes. Into some of these, plugs of phosphorus pentoxide were introduced. A current of oxygen was driven through the tubes, and the ends sealed in the blowpipe flame. It was found necessary that some means should be adopted to prevent the phosphorus pentoxide being shaken to the end of the tube containing the purified phosphorus or carbon. At first loose diaphragms of platinum foil were used, but it was found to be quite sufficient if a bend was made in the tubes. The tubes were then set aside. While the drying was in progress, measures were taken to free the glass as far as possible from adhering moisture, and for this purpose the ends of the tube containing the phosphorus or carbon were placed in an air-bath at a temperature of 130—150°, while the ends containing the phosphorus pentoxide were kept cool.

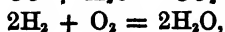
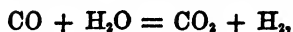
After about eight days, the tube containing phosphorus in the dried oxygen, and a similar tube with phosphorus in oxygen saturated with aqueous vapour, were supported at the same height above the flame of

an Argand burner. Soon the phosphorus in the wet tube burnt with a brilliant flash which filled the tube, while the dry phosphorus began



slowly to distil, and form a red and yellow deposit on the cooler part of the tube. No flash or explosion was seen in the dried tube. The tube containing the carbon in dried oxygen was then arranged with a comparative tube over the large flame of a Bunsen burner. The moist carbon burnt with bright scintillating flashes, but no apparent combustion took place in the dry tube, although it was heated to bright redness for several minutes. These experiments indicated that moisture was necessary for the combustion of both phosphorus and carbon.

I thought it advisable to confine my attention at first to the case of carbon. In 1871 Dubrunfaut, in a short paper (*Compt. rend.*, 1871) read before the French Academy, gave an account of some organic combustions in which he had experienced great difficulty in burning the carbon completely with dry copper oxide and dry oxygen. He concluded that the oxidation of carbon is performed through the intervention of water-vapour. Dumas (*ibid*, 1872) imagining that his experiments on the atomic weight of carbon were called in question, undertook some experiments to refute Dubrunfaut's conclusions. Graphite was purified and heated in a platinum boat in a tube of porcelain. Oxygen, purified by potash and dried by sulphuric acid, was passed over it. All the graphite was burnt, although the oxygen was so dry that 50 litres of it only gave up 7 mgrms. to a weighed sulphuric acid tube. He considers, therefore, that unless Dubrunfaut's hypothesis that aqueous vapour exists in the atmosphere in a state inaccessible to our reagents, is true, carbon must unite directly with oxygen. Dumas' experiments are not conclusive when it is remembered that a very small quantity of water would serve as an efficient carrier of the oxygen to the carbon by an alternate process of reduction and oxidation. In the case of carbon monoxide and oxygen, the equations may be supposed to be



so that one molecule of water would theoretically be sufficient to convert an infinite quantity of carbon monoxide into carbon dioxide.

My aim, therefore, was to reduce the aqueous vapour to so small a limit, that in the time during which the carbon in contact with oxygen was at a red heat, the carbon should not be completely oxidised. This has been accomplished. A large number of experiments were made in the same manner as the first. The tubes containing the purified charcoal in dried oxygen were heated with comparative tubes containing moist oxygen in the flame of the same Bunsen burner. The heating was continued for two minutes after the moist charcoal had begun to burn. In all cases the tubes were heated to redness, and in no case was there visible combustion in the dry tube. The gases were then analysed. The results of some of the analyses are given below.

	Wet.	Dried for 1 week.	Wet.	Dried for 2 weeks.*	Wet.	Dried for 4 weeks.
Carbon dioxide	50·1	15·4	51·0	19·0	45·3	14·1
Carbon monoxide	22·2	20·6	31·2	14·8	32·5	27·8
Oxygen	—	41·3	—	46·1	—	28·2
Nitrogen	27·6	22·6	17·7	20·0	22·1	29·8

	Wet	Dried for 8 weeks.	Wet.	Dried for 12 weeks.	Wet.	Dried for 16 weeks.
Carbon dioxide	23·3	12·5	58·8	15·8	52·4	17·8
Carbon monoxide	60·0	27·5	23·2	24·2	25·2	16·5
Oxygen	—	39·0	—	33·3	—	45·0
Nitrogen	16·6	21·0	17·9	26·6	22·3	20·6

In five out of these six experiments it will be seen that half the oxygen was left uncombined in the dry tubes, whilst none remained in the wet tubes. The burning of carbon, therefore, is retarded by drying the oxygen in which it burns. There is a limit to the drying power of phosphorus pentoxide, so that there is always some water-vapour left, and this always has time to act—several times it may be—while the carbon is red hot. In one experiment, the two tubes were only just heated until the wet carbon began to burn. The analyses of the gases gave—

* This tube was heated for 7 minutes.

	Dry.	Wet.
Carbon dioxide	1·43	22·21
Carbon monoxide	7 13	21·35
Oxygen	72·30	36·31
Nitrogen	19·09	20·12

In order to be able to heat the carbon to redness for a short period, another form of experiment was adopted. A small rod, 2 cm. long, of charcoal purified by heating to redness in chlorine, was enclosed in a coil of fine platinum wire. The ends of this coil were attached to thicker wires, sealed into small glass tubes which passed through the caoutchouc stopper of a small glass globe, 200 c.c. capacity. In the globe was pure oxygen, dried by phosphorus pentoxide. A few drops of mercury covered the caoutchouc stopper. The oxygen was left in contact with the phosphorus pentoxide for 14 days. A current from two Grove's cells was passed for an instant through the wire coil. It was raised to bright redness. The carbon ceased to glow immediately after the current was interrupted; it was then raised to a white heat by a longer application of the current. The carbon glowed for five seconds after the current had ceased. The same current was then applied for an instant to a similar apparatus in which the oxygen was wet. The carbon took fire and burnt with bright scintillations until it was altogether consumed.

At Mr. Dixon's suggestion, another arrangement was used, which did not involve the presence of hot platinum. Instead of the coil in the last experiment, two small carbon rods were attached to the terminals; their resistance, however, was so great that a direct current from a dynamo-electrical machine would not pass through them. By means of a Ruhmkorff coil with four Grove's cells, a succession of sparks could be passed. A discharge was sent between the carbon rods until one was red hot; on stopping the discharge, the glowing ceased. A strong discharge was then sent for half a minute, raising one rod to a white heat. This burnt for a few seconds, and then went out. A similar experiment was tried with wet oxygen, and on the passage of four or five sparks both carbons burnt with bright scintillations.

Water-vapour exerts some influence on the combustion of carbon. Indications have also been obtained of a similar influence on the combustion of sulphur and phosphorus. I hope to be able to pursue my investigations on this subject further.

The experiments recorded in the paper were carried on in the Laboratory of Balliol College, Oxford.

XXXVI.—*The Ortho-Vanadates of Sodium and their Analogues.*

By HARRY BAKER, Berkeley Fellow in the Owens College,
Manchester.

MENDELÉEFF in his *Periodic System* states his opinion that the true analogues of vanadium are chromium and titanium on the one hand, and on the other niobium and tantalum, to which it exhibits a greater resemblance than to phosphorus. Again, Rammelsberg (*Sitzungsber. d. K. Akad. d. Wissensch.*, Berlin, 1883) after describing a great number of alkaline vanadates, comes to the conclusion that "the phosphates cannot be directly compared with the vanadates, although $R''_3P_2O_6$ and $R''_3V_2O_6$, and also $R''_4P_2O_6$ and $R''_4V_2O_6$ are isomorphous," i.e., the minerals of the apatite-group and vanadinite, and the minerals of the liebethenite-group and descloisite. Recently Ditte (*Compt. rend.*, 96, 575—577) has described the preparation of some new members of the apatite and wagnerite-groups of minerals, amongst them being $3(Ca_3V_4O_{18})CaBr_2$ and $Ca_3V_4O_{18}CaBr_2$, which exactly resemble in form the corresponding phosphorus and arsenic compounds. After the replacement of phosphorus by vanadium in the apatite series had been recognised, it was next discovered in the case of a double fluoride and phosphate of sodium formed during the manufacture of caustic soda. No other cases of crystalline compounds in which phosphorus or arsenic is partially or wholly replaced by vanadium are known.

In order to trace the resemblance between the vandanates and phosphates and arsenates, it is evidently necessary to confine one's attention to the tribasic ortho-salts, since acid ortho-salts of vanadium, it would appear, cannot be prepared, and on the other hand, the pyro- and meta-arsenates are not known in the crystalline state. The only tribasic ortho-vanadates soluble in water are those of the two alkali-metals sodium and potassium; and of these only the sodium salt is available, since the potassium salts crystallise with great difficulty.

The tribasic phosphate and arsenate of sodium crystallise each with 12 mols. of water, in the form of hexagonal prisms, whilst the only known tribasic vanadate of sodium is described (Roscoe, *Phil. Trans.*, 1870) as separating with 16 mols. of water, in the form of needle-shaped crystals. It was, however, soon found that a vanadate containing the same quantity of water as the phosphate and the arsenate, and having the same form, could be obtained without any difficulty. Furthermore, less hydrated forms of the vanadate exist, and the phosphate and arsenate corresponding with two of these forms are shown to be formed under the same circumstances; and finally the

pure vanadium compound, corresponding with the double phosphate and fluoride of sodium, already mentioned, is described.

I. *Sodium Ortho-vanadate*, $\text{Na}_2\text{VO}_4 \cdot 12\text{H}_2\text{O}$.—This salt is readily obtained by adding an excess of caustic soda to a solution of sodium pyrophosphate, and also by igniting vanadic acid with sodium carbonate, and crystallising the product from water or caustic soda solution. The salt is very soluble in water, but much less so in caustic soda solutions.

It crystallises in longer or shorter hexagonal prisms, terminated with the basal plane; occasionally traces of a rhombohedron are present. The optical behaviour is that of a hexagonal crystal; sections parallel to the base show a normal uniaxial interference figure; it is positive. The following refractive indices were determined on crystals with ground and glazed faces:—

	o.			e.		
	Li.	Na.	Tl.	Li.	Na.	Tl.
Crystal No. 1	1.5044	1.5099	1.5151	1.5177	1.5238	1.5296
„ 2	1.5035	1.5092	1.5148	1.5170	1.5228	1.5290
Mean	1.5040	1.5095	1.5150	1.5173	1.5232	1.5293

The analyses of this and the following salts were effected as follows:—The water was determined by simple ignition and loss of weight; in the residue, or in the original substance, the vanadium could be determined by titration with potassium permanganate. The vanadic, phosphoric, or arsenic acids were removed from another portion by precipitation generally as silver salts; the washed precipitates were dissolved in nitric acid, the silver precipitated by hydrochloric acid, and in the filtrate the vanadic acid determined by simple evaporation and ignition, or the phosphoric or arsenic acids by precipitation with magnesia mixture; the weight of silver chloride was also used to calculate the amount of these acids. The filtrate from the silver vanadate, &c., after removal of excess of the reagent by means of ammonium chloride, or sulphide, was used for estimating either the sodium by evaporation with sulphuric acid and ignition, or the fluorine by precipitation with calcium chloride.

For analysis, moderately large crystals were employed, and were freed from solution either by washing with dilute alcohol or by means of filter-paper, by which they were also dried. The analytical data are—

Preparation 1.—0.6280 gram substance lost 0.3296 gram water =

52.48 per cent., and 0.6908 gram substance required 20.3 c.c. permanganate (1 c.c. = 0.007772) = 22.83 per cent. vanadic oxide.

Preparation 2.—1.1438 gram substance gave 1.2416 gram AgCl = 23.04 per cent. vanadic oxide, and 0.6419 gram sodium sulphate = 24.51 per cent. sodium oxide.

Preparation 3.—0.9680 gram substance gave 0.5415 gram sodium sulphate = 24.43 per cent. sodium oxide, and 0.2206 gram vanadic oxide, requiring 110.6 c.c. permanganate (1 c.c. = 0.002002) and 1.0540 gram silver chloride = 22.79, 22.89, and 23.11 per cent. vanadic oxide respectively.

0.5290 gram substance left 0.2531 gram residue = 52.16 per cent. water.

1.1157 gram substance left 0.5323 gram residue = 52.20 per cent. water.

0.6963 gram substance required 78.9 c.c. permanganate = 22.70 per cent. vanadic oxide.

	$\text{Na}_3\text{VO}_4 \cdot 12\text{H}_2\text{O}$.	Found.						Mean.
V_2O_5	22.81	22.83	23.04	22.79	22.89	23.11	22.70	22.89
Na_2O	23.25	—	24.51	24.43	—	—	—	24.47
H_2O	53.94	52.48	—	52.16	52.20	—	—	52.24
	100.00							

Although these data are sufficient to show the composition of the body, it is to be noted that the mean sodium per cent. is 1.22 too high, and the water 1.66 per cent. too low. This is due to the salt containing mechanically admixed caustic soda, and the amount of the error may be determined by precipitating the solution of the salt with barium chloride, and determining the alkalinity of the filtrate, which is quite free from vanadium. The sample No. 3, although it had been washed thoroughly with dilute alcohol, was found to contain caustic soda equivalent to 1.14 per cent. sodium oxide; after recrystallisation it contained 1.56—1.60 per cent.

The corresponding phosphate and arsenate being well known, it only remains to compare the determinations of the refractive indices and to remark that in their analysis the same difficulty is encountered as with the vanadate, although to a less extent. The crystalline form of both compounds is exactly that of the vanadate, but the arsenate generally forms much longer and thinner crystals. A crystal of the vanadate continues its growth in a solution of the phosphate, and a minute crystal of any one of the three salts will immediately cause a

supersaturated solution of either of the other salts to commence crystallising. The optical character is positive—

	Li.	Na.	Tl.
$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O} \dots \left\{ \begin{array}{l} o \dots \\ e \dots \end{array} \right.$	—	1.4486	—
	—	1.4539	—
$\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O} \dots \left\{ \begin{array}{l} o \dots \\ e \dots \end{array} \right.$	1.4553	1.4589	1.4624
	1.4630	1.4669	1.4704

While making the preceding vanadate, the formation of other crystals was frequently noticed, and since the solutions employed in such cases were either very concentrated or contained much caustic soda, it appeared probable that they were forms of the tribasic vanadate containing less water of crystallisation. This is borne out by the subsequent observations.

The following three salts are all prepared from solutions of sodium ortho-vanadate by concentration and cooling, or by the addition of caustic soda, which acts as a dehydrating agent, and also renders the salts more insoluble. The solubility of these salts being considerable and greatly influenced by slight changes of temperature, no detailed directions for obtaining them can be given, and although their formation may be easily watched under the microscope—the different hydrates being at once recognised by their crystalline forms—their preparation in quantity remains a matter of trial and experience. A great difficulty is the removal of the mother-liquor, which, as regards the most stable salt, $\text{Na}_3\text{VO}_4 \cdot 12\text{H}_2\text{O}$, is always in a state of supersaturation, and thus ready to solidify on the slightest provocation; in the preparation of the lowest hydrate, $\text{Na}_3\text{VO}_4 \cdot 8\text{H}_2\text{O}$, this difficulty is almost insurmountable.

The salt, $\text{Na}_3\text{VO}_4 \cdot 10\text{H}_2\text{O}$, exists in two distinct modifications, differing in their crystalline form, one appearing as rhombic dodecahedrons and being easily obtained, the other appearing as hexagonal plates, and not so often observed.

II. *Sodium Ortho-vanadate*, $\text{Na}_3\text{VO}_4 \cdot 10\text{H}_2\text{O}$. *Regular*.—The crystals are limpid, well-formed rhombic dodecahedrons with occasional faces of the octahedron. They are isotropic. The refractive index was determined on ground and glazed crystals—

Li.	Na.	Tl.
1.5244	1.5305	1.5366

The sample for analysis was dried by pressure between papers. 0.9972 gram substance lost on ignition 0.4929 gram = 49.43 per cent. water, and gave 0.2582 gram vanadic oxide = 25.89 per cent., and 0.5899 gram sodium sulphate = 25.83 per cent. sodium oxide—

	$\text{Na}_3\text{VO}_4 \cdot 10\text{H}_2\text{O}$.	Found.
V_2O_5	25·07	25·89
Na_2O	25·53	25·83
H_2O	49·41	49·43
	100·01	

III. *Sodium Ortho-vanadate*, $\text{Na}_3\text{VO}_4 \cdot 10\text{H}_2\text{O}$. *Hexagonal*.—This salt, having almost the same form as the pyrovanadate, $\text{Na}_4\text{V}_2\text{O}_7 \cdot 18\text{H}_2\text{O}$, was at first mistaken for the latter; the crystals of the ortho-vanadate are, however, thicker than the pyrovanadate. The forms are simply ∞P , 0P , and the habitus thin tabular; the crystals exhibit a uniaxial interference figure; they are positive. The refractive index was determined upon ground and glazed crystals—

	<i>o</i> .			<i>e</i> .		
	Li.	Na.	Tl.	Li.	Na.	Tl.
Crystal No. 1	1·5327	1·5396	1·5161	1·5403	1·5473	1·5536
" 2	1·5336	1·5399	1·5460	1·5413	1·5478	1·5538
" Mean	1·5332	1·5398	1·5460	1·5408	1·5475	1·5537

For analysis the crystals were dried between papers. .

0·4810 gram substance lost 0·2378 gram water = 49·44 per cent., and required 31·9 c.c. permanganate (1 c.c. = 0·003858) = 25·59 per cent. vanadic oxide. A portion of the same sample was analysed after exposure to the air. 0·5590 gram substance required 36·1 c.c. permanganate = 24·91 per cent. vanadic oxide; 0·7642 gram substance lost 0·3785 gram water = 49·53 per cent., and required 50·3 c.c. permanganate = 25·39 per cent. vanadic oxide. Again, 0·7500 gram substance gave 0·4402 gram sodium sulphate = 25·63 per cent. sodium oxide, 0·8738 gram silver chloride, and 0·1921 gram vanadic oxide = 24·73 and 25·61 per cent. vanadic oxide respectively—

	$\text{Na}_3\text{VO}_4 \cdot 10\text{H}_2\text{O}$.	Found.				
V_2O_5	25·07	25·59	24·91	25·39	24·73	25·61
Na_2O	25·53	—	—	—	25·63	—
H_2O	49·41	49·44	—	49·53	—	—
	100·01					

IV. *Sodium Ortho-vanadate*, $\text{Na}_3\text{VO}_4 \cdot 8\text{H}_2\text{O}$ (P).—This salt separates in apparently rhombic plates, sometimes rectangular in outline, some-

times octangular through the presence of an obtuse prism whose obtuse angle measures $122-128^\circ$. The crystals are frequently very minute, but at other times rather large; they do not show any axial interference figure, but depolarise parallel light like a rhombic crystal.

The isolation of the thin flat plates from the mother-liquor is extremely difficult; placed on paper to drain, the whole at once begins to solidify; the only method is to pour off the liquid carefully and replace it by dilute alcohol of such strength that no precipitation can take place, to pour off this liquid, and replace it by fresh alcohol of suitable strength, and so on, but the crystals must not be stirred or broken until all the mother-liquor is removed.

After many attempts, only two approximate analyses could be made; the numbers show clearly that the salt contains much less water of crystallisation than the preceding salts, but the exact amount remains doubtful:—

	$\text{Na}_3\text{VO}_4, 8\text{H}_2\text{O}$.	Found.	
V_2O_5	27.81	28.79	27.50
Na_2O	28.35	—	27.69
H_2O	43.84	41.86	44.81
	100.00		

The phosphates and arsenates corresponding with the last three vanadates do not appear to have been previously obtained; the existence of two of them, viz., $\text{Na}_3\text{PO}_4, 10\text{H}_2\text{O}$ regular, and $\text{Na}_2\text{AsO}_4, 10\text{H}_2\text{O}$ regular, and $\text{Na}_3\text{PO}_4, 8\text{H}_2\text{O}$ (?), and $\text{Na}_3\text{AsO}_4, 8\text{H}_2\text{O}$ (?) are easily demonstrated by the use of the microscope, their forms being exactly those of the corresponding vanadates. They have not been prepared in quantity.

V. *Sodium Vanadofluoride*, $2\text{Na}_3\text{VO}_4, \text{NaF}, 19\text{H}_2\text{O}$, is formed by fusing together the requisite quantities of vanadic acid, sodium carbonate, and sodium fluoride, and crystallising the product from warm water, or by adding sodium fluoride in calculated quantity to a solution of trisodic orthovanadate, or to one of sodium pyrovanadate mixed with excess of caustic soda. From any of these solutions, the salt crystallises in limpid octohedrons, which may be recrystallised without change from a very dilute caustic soda solution. The crystals do not act on polarised light; they belong to the regular system; their form is that of the octohedron, or the same modified by the rhombic dodecahedron; crystallised rapidly it forms skeletons derived from

the preceding two forms. The refractive indices were determined on ground and glazed crystals:—

	Li.	Na.	Tl.
Crystal No. 1.....	1.5176	1.5235	1.5290
„ 2.....	1.5165	1.5224	1.5277
Mean	1.5171	1.5230	1.5284

For analysis the crystals were dried between papers.

Preparation 1.—0.9443 gram substance gave 0.6208 gram sodium sulphate = 28.72 per cent. sodium oxide, and 1.0701 gram silver chloride and 0.2312 gram vanadic oxide = 24.06 and 24.48 per cent. vanadic oxide respectively; 1.2625 gram substance lost 0.5704 gram water = 45.17 per cent.; 1.3429 gram substance gave 0.072 gram calcium fluoride = 2.61 per cent. fluorine.

Preparation 2.—Analyses made by Mr. A. Siebold. 1.6893 gram substance gave 0.081 gram calcium fluoride and 1.8370 gram substance gave 0.0868 gram calcium fluoride = 2.34 and 2.30 per cent. fluoride; 1.0090 gram substance gave 1.1454 gram silver chloride = 24.12 per cent. vanadic oxide; 1.1685 gram substance gave 0.7700 gram sodium sulphate = 28.77 per cent. sodium oxide and 0.2860 gram vanadic oxide = 24.47 per cent.; 0.6960 gram substance required 47.5 c.c. permanganate (1 c.c. = 0.003555) = 24.26 per cent. vanadic oxide; 1.2932 gram substance lost 0.5852 gram water = 45.25 per cent.

	2Na ₃ VO ₄ .NaF.19H ₂ O.	Found.				
V ₂ O ₅ ...	24.27	24.06	24.48	24.12	24.47	24.26
Na 21.42 = Na ₂ O 28.87		28.72	—	28.77	—	—
O	6.37	—	—	—	—	—
F	2.52	2.61	—	2.34	2.30	—
H ₂ O ...	45.42	45.17	—	45.17	—	—
	100.00					

A salt could not be obtained containing a larger quantity of fluorine. The crystals of the corresponding phosphate obtained during the manufacture of caustic soda contained up to 1.28 per cent. vanadic oxide, and the artificial salt, prepared by Rammelsberg—and to which 18 mols. of water only are ascribed—3.39 per cent.

The corresponding phosphofluoride and arsenofluoride were first prepared by Briegleb (*Annalen*, 1856, 95), but he ascribed to them the incorrect formulæ Na₃PO₄.NaF.12H₂O and Na₃AsO₄.NaF.12H₂O. In 1864 Rammelsberg (*J. pr. Chem.*, 94, 237) first examined the small red crystals obtained in the soda manufacture, and supposed them to be a double phosphate and silicate of sodium, which by recrystallisation is decomposed and converted into a new hydrate of

sodium phosphate, viz., $\text{Na}_3\text{PO}_4 \cdot 10\text{H}_2\text{O}$. That this last salt contains fluorine and is a fluorophosphate was admitted in 1880 (*Monatsh. Akad. Berl.*, 1880, 777); but it is then described as containing only 18 instead of 19 mols. of water, i.e., $2\text{Na}_3\text{PO}_4 \cdot \text{NaF} \cdot 18\text{H}_2\text{O}$. In 1865 Baumgarten (*Zeit. f. Chem.*, N.S., 1, 605) re-examined the octohedrons from the soda manufacture, ascribing to them the formula $4\text{Na}_3\text{PO}_4 \cdot \text{Na}_2\text{SiO}_3 \cdot 2\text{NaF} \cdot 40\text{H}_2\text{O}$; by recrystallisation they lost their silica and were converted into $2\text{Na}_3\text{PO}_4 \cdot \text{NaF} \cdot 19\text{H}_2\text{O}$; this last salt, as well as another, $2\text{Na}_3\text{PO}_4 \cdot \text{NaF} \cdot 22\text{H}_2\text{O}$, he also obtained by synthesis, but was unable to obtain a compound having the composition described by Briegleb. The crystals from the soda liquors were again examined in 1872 by Thorpe (this Journal [2], 10, 660) who found them to have a composition expressed exactly by Baumgarten's formula $2\text{Na}_3\text{PO}_4 \cdot \text{NaF} \cdot 19\text{H}_2\text{O}$.

I have confirmed the preparation of the salt with 19 mols. of water by Baumgarten's method, but the salt with 22 mols. of water could not be obtained; a water determination gave 48.10 per cent., which agrees exactly with the calculated quantity for the 19 mol. hydrate, viz., 48.01 per cent.

Thus no less than six different formulæ have been proposed for the sodium phosphofluoride, and in every case the crystals analysed were regular octohedrons. Coupling this with the contrary statements and the analyses here given, it follows that only one fluorophosphate is known, viz., $2\text{Na}_3\text{PO}_4 \cdot \text{NaF} \cdot 19\text{H}_2\text{O}$; for neither Briegleb's salt nor Baumgarten's $2\text{Na}_3\text{PO}_4 \cdot \text{NaF} \cdot 22\text{H}_2\text{O}$ can be obtained by the methods given for their preparation, and that the crystals from the soda liquors have the composition $2\text{Na}_3\text{PO}_4 \cdot \text{NaF} \cdot 19\text{H}_2\text{O}$ has been shown by Thorpe.

Further, it follows from the correction of Briegleb's formula for the phosphorus salt, that the isomorphous arsenic compound must have the composition $2\text{Na}_3\text{AsO}_4 \cdot \text{NaF} \cdot 19\text{H}_2\text{O}$, and not $\text{Na}_3\text{AsO}_4 \cdot \text{NaF} \cdot 12\text{H}_2\text{O}$; this is confirmed by the annexed analysis.

Sodium arsenofluoride was prepared from a solution containing sodium arsenate, sodium fluoride, and caustic soda. The crystals are brilliant octohedrons, and are isotropic.

	$2\text{Na}_3\text{AsO}_4 \cdot \text{NaF} \cdot 19\text{H}_2\text{O}$.	Found.			
As_2O_5	28.77	28.97	29.22	28.82	28.97
Na	20.15	20.26	—	—	—
O	5.99	—	—	—	—
F	2.37	2.26	—	—	—
H_2O	42.72	42.68	42.74	42.80	—
	100.00				

That the phospho-, arseno-, and vanado-fluorides of sodium form an isomorphous series is seen from their composition, their form, and from the observation that a crystal of the vanadate continues its growth unimpeded in solutions of either the phosphate or of the arsenate, and also a mixture of equal parts of the phosphate and vanadate deposited crystals containing both phosphoric and vanadic acids, viz., 11.42 and 11.68 per cent. of the latter, 24.27 per cent. being contained in the pure vanadate.

A comparison of the refractive indices of the phosphofluoride and arsenofluoride with those of the vanadofluoride show that in this series of salts, as in the series $\text{Na}_3\text{XO}_4, 12\text{H}_2\text{O}$, the vanadium compound has a greater refractive and dispersive power than either the phosphorus or arsenic compounds:—

	Li.	Na.	Tl.
$2\text{Na}_3\text{PO}_4, \text{NaF}, 19\text{H}_2\text{O}$	1.4489	1.4519	1.4545
$2\text{Na}_3\text{AsO}_4, \text{NaF}, 19\text{H}_2\text{O}$	1.4657	1.4693	1.4726

The annexed series of crystalline ortho-phosphates, vanadates, and arsenates are thus known, and the conclusion follows that the crystalline ortho-vanadates, so far as they are known, do correspond exactly in composition and in form with the ortho-phosphates and arsenates:—

Hexagonal. . . .	$\text{Na}_3(\text{P or V or As})\text{O}_4, 12\text{H}_2\text{O}$.
Regular.	$\text{Na}_3(\text{P or V or As})\text{O}_4, 10\text{H}_2\text{O}$.
Hexagonal. . . .	$\text{Na}_3\text{V}(\text{? P or As})\text{O}_4, 10\text{H}_2\text{O}$.
Rhombic	$\text{Na}_3(\text{P or V or As})\text{O}_4, (\text{?})8\text{H}_2\text{O}$.
Regular.	$2\text{Na}_3(\text{P or V or As})\text{O}_4, \text{NaF}, 19\text{H}_2\text{O}$.

XXXVII.—*The Formation of Hyponitrites from Nitric Oxide.*

By EDWARD DIVERS and TAMEMASA HAGA.

NITRIC oxide is slightly absorbed by a strongly alkaline solution of potassium stannite, converting it into stannate. After passing the gas for about two hours, the solution begins to effervesce slightly, especially when shaken, and continues to do so as long as the current of nitric oxide is maintained and for hours afterwards. The reaction takes place so slowly that even when our experiments lasted for two or three days, some stannite still remained unconverted to stannate.

The slowness of the change and the very slight effervescence, com-

bined with the circumstance that the nitric oxide employed is never quite pure, have prevented us from ascertaining the nature of the gaseous product of the reaction, but we believe from analogy that it is nitrous oxide. Either this or nitrogen it must certainly be. In the solution, we found a hyponitrous compound in small quantity, a very little ammonia, and traces of hydroxylamine.

Solution of potassium stannite was prepared by mixing stannous chloride solution with sodium carbonate, allowing the precipitate to subside in a closed vessel, decanting the supernatant mother-liquor as far as possible, and adding some solid potassium hydroxide to the residue. A solution was thus obtained which contained alkali chloride, and, even in the cold, deposited some black stannous oxide.

A slow and continuous stream of nitric oxide washed with alkali was passed into this solution, hydrogen being passed through the flask both before and after this treatment, in order to avoid all contact between the nitric oxide and air within the apparatus. One of two methods of treatment was now followed : either silver nitrate or barium chloride was added.

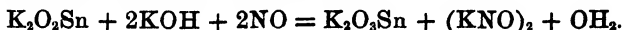
The addition of silver nitrate causes a succession of precipitates. First, there is a black precipitate produced by the unchanged stannite and by a trace of hydroxylamine ; then, a white precipitate of chloride ; next, a dirty grey one ; and then a brown one of silver oxide. After this would come, no doubt, silver stannate, but we have not pursued the matter further, the dirty grey precipitate yielding us what we were seeking. The black precipitate which first comes down will not be produced if the solution is previously stirred with precipitated mercuric oxide, which oxidises both the remaining stannite and the trace of hydroxylamine.

The dirty grey precipitate, mixed with a little silver chloride and oxide formed before and after it, was collected apart, thoroughly washed, treated with dilute nitric acid, and the acid solution filtered and neutralised with ammonia. A bright yellow precipitate was thus obtained decomposable by hot acids, and showing the other characters of silver hyponitrite. No trace of phosphate was with it.

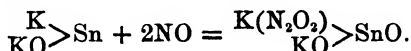
The addition of barium chloride to the solution which has been treated with nitric oxide, gives an amorphous white precipitate of a composite nature. If this is removed and the filtrate left to stand after addition of more barium chloride, a second crystalline precipitate slowly forms, which is converted by silver nitrate into tolerable pure silver hyponitrite. The first-formed barium precipitate after slight washing, is changed to a dirty grey-brown precipitate by silver nitrate. This when treated like that formed in the original solution by silver nitrate also yields silver hyponitrite. The total hyponitrite obtained is but small in amount, even under the most

favourably conditions of a long treatment with nitric oxide, and a nearly complete conversion of the stannite to stannate.

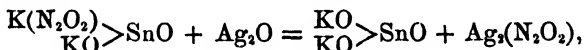
The reaction between the potassium stannite and the nitric oxide may be represented by the equation—



But, if we seek for a fuller insight into this reaction, we may possibly find it by taking into consideration the continual though slight effervescence which occurs in the solution, together with what happens under similar circumstances on passing nitric oxide into an alkaline solution of potassium sulphite, when much such an effervescence may also be observed. In that case nitrososulphate is formed, and in the present case it seems probable, therefore, that a *nitrosostannate* is the compound which is produced and afterwards, like the nitrososulphate, converted into hyponitrite. Its production will take place thus:—



Then the nitrosostannate must give hyponitrite with silver oxide:—



although nitrososulphates are incapable of undergoing such a change. If this explanation of what happens is correct, the dirty grey precipitate which yields hyponitrite will be silver nitrosostannate, and the effervescence will be due to the decomposition of the potassium nitrosostannate into stannate and nitrous oxide:—



a decomposition similar to that of the nitrososulphate.

According to our own experience, there are now known three distinct reactions by which hyponitrites can be formed: (1) that between amalgams of the alkali-metals and a nitrite (or nitrate); (2) that between these amalgams and a nitrososulphate; (3) and that between alkali stannites and nitric oxide in presence of free alkali afterwards acidified. According to Zorn's observations, a fourth reaction is that between ferrous hydroxide and a nitrite (or nitrate) in neutral or slightly acid solution.

Inaction of Alkali Stannites with Nitrites and Nitrates.

Neither nitrites nor nitrates undergo any change that we have succeeded in detecting, when they are treated with alkali stannite in presence of alkali hydroxide, even in hot solution. Acid solutions of stannous chloride react with nitrites and nitrates (v. Dumreicher).

Ferrous Hydroxide, and its Behaviour with Nitric Oxide, Nitrites, and Nitrates in Alkaline Solution.

Ferrous hydroxide, as commonly prepared, is a bulky, gelatinous, greenish-grey substance, exceedingly liable to oxidation, and then forming the greenish-black magnetic hydroxide which changes to red ferric hydroxide on further oxidation. If, however, after precipitation the supernatant mother-liquor is poured off and solid potassium hydroxide dissolved in the remaining mother-liquor, the ferrous hydroxide diffused through it undergoes in the course of a few hours a very considerable diminution in volume, and then forms a pale greenish-grey pulverulent precipitate, although the gelatinous precipitate may have been of a much darker colour. This dense hydroxide is much more stable, and in oxidising does not form the black hydroxide before becoming ferric hydroxide.

Such ferrous hydroxide mixed with solution of potassium hydroxide was treated for hours with nitric oxide gas. In this way the ferrous hydroxide became oxidised to ferric hydroxide, and the nitric oxide converted largely into ammonia. Neither hydroxylamine nor hyponitrite could be detected as products of this reaction.

Alkali nitrites also yielded much ammonia when treated with the mixed ferrous and potassium hydroxides, but neither hyponitrite, hydroxylamine, nor any gaseous product. Alkali nitrates were not changed in the least by the same mixture

XXXVIII.—*The Existence of Barium and Lead Nitrososulphates*

By EDWARD DIVERS and TAMEMASA HAGA

THE nitrososulphates of potassium, sodium, and ammonium have each been prepared by the union of nitric oxide with the sulphite in alkaline solution. But these salts have hitherto appeared to be incapable of undergoing regular double decomposition with other salts. Thus, in contact with copper sulphate they instantly change to alkali sulphate and nitrous oxide, whilst they do not react at all with copper hydroxide. With silver nitrate, their decomposition does not commence immediately, even when this reagent is in concentrated solution and the alkali nitrososulphate is in crystals, but after a short time an action begins, and then proceeds very rapidly.

It is possible, however, to effect some double decompositions of

these nitrososulphates. Baryta-water, which does not precipitate them when it is dilute, gives when concentrated an abundant white precipitate, without causing any effervescence. The precipitate is soluble in water, and, when drained from its mother-liquor on a porous tile, effervesces freely in contact with hydrochloric acid, barium sulphate being formed at the same time. The nitrososulphate with which we experimented was an aqueous solution of the pure potassium salt. The lead salt mixed with hydroxide may be obtained as a white insoluble substance by adding a solution of basic lead acetate to a solution of nitrososulphate; after precipitation, the mother-liquor no longer effervesces with acids. Treated, itself, with dilute nitric acid it momentarily dissolves, but is almost immediately replaced by lead sulphate, while effervescence occurs. We have failed to prepare the calcium salt by adding to a nitrososulphate a solution of lime in sugar-water.

XXXIX.—*Preparation of Ethylene Chlorothiocyanate and β -Chlorethylsulphonic Acid.*

By J. WILLIAM JAMES, University College, Cardiff.

IN former numbers of this Journal (Trans., 1879 and 1883) I have described the preparation of ethylene chlorothiocyanate by digesting an alcoholic solution of ethylene chlorobromide with potassium thiocyanate, filtering from the potassium bromide, and distilling the alcoholic liquid until the thermometer rose to 120° . After removing the ethylene dithiocyanate, which is always formed, the oil was distilled under ordinary pressure.

I have since found that a much better yield can be obtained by distilling under diminished pressure, although the sudden decomposition which takes place near the end of the distillation cannot be prevented. By using a suitable apparatus, however, the pure compound can be collected without becoming contaminated by the decomposition-products. A T-tube with two glass taps answers the purpose, one end of the horizontal tube being connected with the retort, the other with the receiver. As soon as decomposition commences the tap near the receiver is quickly closed, and the one in the vertical tube opened, thus permitting a free exit for the products.

During the distillation, the taps should be frequently moved to ensure that they do not become fixed. A pressure of about 400 mm.

was used, and I have pretty constantly obtained 35 grams of ethylene chlorothiocyanate from 100 grams of pure ethylene chlorobromide boiling at 106—108°, or nearly 42 per cent of the theoretical yield.

If distilled under ordinary pressure, the $C_2H_4Cl.SCN$ is liable to contain small quantities of $C_2H_4(SCN)_2$, but if prepared as above described a pure product is obtained, as the following experiment will show:—

100 grams of ethylene chlorothiocyanate so obtained were oxidised with concentrated nitric acid, and after removal of excess of the latter by evaporation the chlorethylsulphonic acid remaining was neutralised with lead carbonate. On concentrating the filtrate on the water-bath, the lead salt crystallised in prisms apparently of the oblique system.

An analysis showed them to be pure lead chlorethylsulphonate, containing 2 mols. H_2O .

Calculated for		Found.	
$(C_2H_4ClSO_3)_2Pb + 2H_2O$.		I.	II.
Pb	38·82	38·73	38·85
$2H_2O$	6·80	6·95	7·07

The mother-liquor was now concentrated, and on cooling it set to a mass of nodular crystals mixed with a few of the other variety. These were separated mechanically, and after pressing between filter-paper, an analysis proved them to be the pure lead salt, but without water of crystallisation.

Calculated for		Found.	
$(C_2H_4ClSO_3)_2Pb$.		I.	II.
Pb	41·85	42·39	42·41

Dittrich (*J. pr. Chem.* [2], 18) could only obtain this salt in the latter form.

When preparing chlorethylsulphonic acid from this salt by means of sulphuretted hydrogen, I have not succeeded in removing all the lead. Even when precipitated in very dilute solution, traces of the lead salt still remain undecomposed. This has not at all interfered with the preparation of the taurine-derivatives, as on neutralising the acid with the amine the lead hydroxide can be got rid of by filtration.

The only way of preparing the pure acid is by acting on the barium salt with sulphuric acid.

XL.—*Derivatives of Taurine.* Part I.

By J. WILLIAM JAMES, Ph.D., F.C.S., University College of South Wales, Cardiff.

Action of Primary, Secondary, and Tertiary Monamines on their respective Salts of β -Chlorethylsulphonic Acid.

TAURINE was synthesised by Kolbe in 1863, by heating either the silver or ammonium salt of β -chlorethylsulphonic acid with excess of ammonia. Some years later, Dittrich succeeded in preparing methyltaurine from the methylamine salt of the above acid and excess of methylamine (*J. pr. Chem.* [2], 18).

Since it has been shown that the necessary chlorethylsulphonic acid may be readily obtained by oxidation of ethylene chlorothiocyanate (*Trans.*, 1879, 806), a further study of the derivatives of so interesting a body as taurine seemed desirable.

Taurine, which from its synthetical formation is β -amidoethylsulphonic acid, $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$, is the most important sulphonic analogue of glycocine (amidoacetic acid), and as di-substituted amidoacetic acids are not known in the free state, but only in combination with HI or HCl (Kraut and Hartmann, *Annalen*, 133, 103), the preparation of a dimethyltaurine or diethyltaurine would have more than ordinary interest. The preparation of a trimethyl-derivative of taurine also offered considerable attraction, as by its reactions some insight would probably be obtained as to its constitution, *i.e.*, whether it should be regarded as the methyl ether of dimethyltaurine,

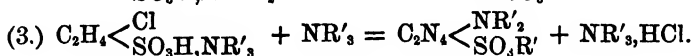
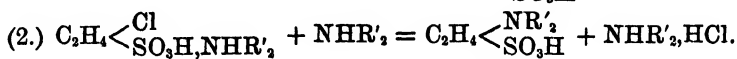
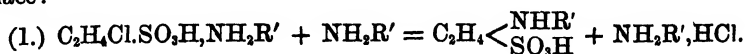
$\text{NMe}_2\cdot\text{C}_2\text{H}_4\cdot\text{SO}_2\cdot\text{OMe}$, or a body of the formula $\begin{array}{c} \text{CH}_2\cdot\text{NMe}_2 \\ | \\ \text{CH}_2-\text{SO}_2 \end{array} \text{O}$. I hope to discuss this in a future communication.

I have investigated the action of mono-, di-, and tri-amines on their respective salts of β -chlorethylsulphonic acid, with most satisfactory results.

General Method for the Preparation of Mono-, Di-, and Tri-substituted Taurines.

The following experiments will show that mono-, di-, and tri-substituted taurines with monad positive radicles can be readily prepared by means of a general method, and as it will considerably curtail subsequent description I will describe it before giving the experimental details.

It consists in heating the amine salt of β -chlorethylsulphonic acid with the necessary quantity of amine in a closed tube for 10 hours at a temperature of 160° , when the following general reactions take place:—



In the case of mono- and di-substituted taurines, excess of barium hydroxide is added to decompose the hydrochloride, and the liberated amine distilled off in a current of steam, after which the mixture is poured into the calculated quantity of boiling dilute sulphuric acid. On filtering, and evaporating the liquid repeatedly with addition of water until all hydrochloric acid is removed, the substituted taurine is obtained in the crude state, and may be purified by crystallisation from water or alcohol as the case may be.

The trimethyl-derivative is easily decomposed by alkalis, and another method has to be employed for removing the trimethylamine hydrochloride.

Ethyltaurine, $\text{NHEt.C}_2\text{H}_4.\text{SO}_3\text{H}$.

10 grams of ethylamine in 33 per cent. aqueous solution were neutralised with a dilute solution of β -chlorethylsulphonic acid prepared from its lead salt with sulphuretted hydrogen. After filtering from a small quantity of lead hydroxide (see p. 366), the liquid was evaporated to a syrup; on cooling, this set to a mass of silky needles, which are extremely deliquescent.

20 grams of the salt were then treated as described under the general method with 5 grams of ethylamine 33 per cent. solution in water. The crude ethyltaurine is exceedingly difficult to purify, the sulphur estimation giving too high, and the nitrogen too low a result. By pouring absolute alcohol on the surface of its aqueous solution evaporated to a syrupy consistency, it may be obtained in the crystalline state. A sample which had been crystallised four times gave the following numbers on analysis, after drying at 110° :—

I. 0.102 gram substance gave 0.0601 gram Pt.

II. 0.214 " " 0.3290 " BaSO₄.

		Found.	
		I.	II.
Calculated for $\text{NH}(\text{C}_2\text{H}_5).\text{C}_2\text{H}_4.\text{SO}_3\text{H}$.			
N	9.15	8.67	—
S	20.91	—	21.02

Ethyltaurine crystallises from water in fine prisms (rhombic?), but contains no water in combination. It has a bitter sooty taste; melts at 147° . Its aqueous solution has an acid reaction.

A specimen of ethyltaurine was also prepared from the silver salt of chlorethylsulphonic acid and excess of ethylamine. The yield is poor, and ethylamine hydrochloride and metallic silver are produced, which necessitates the ultimate use of barium hydroxide.

Allyltaurine, $\text{NH}(\text{C}_3\text{H}_5)\cdot\text{C}_2\text{H}_4\cdot\text{SO}_3\text{H}$.

10 grams of the allylamine salt, which is deliquescent, were treated with the calculated quantity of an aqueous solution of allylamine. The crude allyltaurine was well ground in a mortar with cold strong alcohol, which removes nearly all the brown colouring matter, leaving a white residue. This was dissolved in boiling 90 per cent. alcohol, and, on cooling, the solution deposited fine long prisms. Two sulphur estimations showed that these were not yet pure (III). They were therefore crystallised three times from strong alcohol, and dried at 110° , when the following analytical results were obtained:—

- I. 0.2171 gram substance burnt with CuO , PbCrO_4 , and Cu gave 0.1310 gram H_2O and 0.2886 gram CO_2 .
 II. 0.2210 gram substance by soda-lime method gave 0.1300 gram Pt.

		Found.		
		I.	II.	III.
Calculated for $\text{C}_5\text{H}_9\cdot\text{HN}\cdot\text{C}_2\text{H}_4\cdot\text{SO}_3\text{H}$.				
C	36.4	36.2	—	—
H	6.7	6.7	—	—
N	8.5	—	8.4	—
S	19.3	—	—	20.1; 20.1
O	29.1	—	—	—
<hr/>				
100.0				

Allyltaurine is very easily soluble in water, but only sparingly in strong alcohol. It crystallises from alcohol in beautiful rhombic prisms. It melts at 190 — 195° , and has a slightly bitter taste. Its reaction with litmus is acid.

Phenyltaurine, $\text{NHPh}\cdot\text{C}_2\text{H}_4\cdot\text{SO}_3\text{H}$.

The phenylamine salt of β -chlorethylsulphonic acid was readily prepared by acting on the acid with excess of aniline, which excess was afterwards removed in a current of steam. It crystallises from water in large colourless needles, which on exposure to air do not deliquesce, but become of a fine pink colour.

20 grams of this salt were heated in sealed tubes with 8 grams of aniline and a little water. The crude phenyltaurine finally obtained after several crystallisations from water was air-dried and analysed.

- I. 0.2216 gram burnt with CuO , PbCrO_4 , and Cu produced 0.1153 gram H_2O and 0.3864 gram CO_2 .
 II. 0.1704 gram fused with KHO and KNO_3 gave 0.202 gram BaSO_4 .

	Calculated for $\text{C}_6\text{H}_5\text{HN.C}_2\text{H}_4\text{SO}_3\text{H}$.	Found.	
		I	II
C	47.7	47.5	—
H	5.5	5.7	—
S	15.9	—	16.2

Phenyltaurine is moderately soluble in water, the solution becoming red. It crystallises from water in beautiful thin silky leaves without water of crystallisation. It is sparingly soluble in strong alcohol, and, on cooling, separates in microscopic crystals, apparently rhombic prisms. It has a strongly acid reaction and taste, and dissolves copper hydroxide easily. It melts with decomposition at $277\text{--}280^\circ$. Its aqueous solution gives an intense violet coloration with a solution of bleaching powder, even when very dilute. Ferric chloride produces no marked colour until warmed; the liquid then becomes green, gradually turning to indigo-blue. An attempt to prepare a nitroso-derivative gave an unsatisfactory result.

Phenyltaurine is also easily prepared by heating aniline chlorethylsulphonate with aniline under the ordinary pressure.

Dimethyltaurine, $\text{NMe}_2\text{.C}_2\text{H}_4\text{.SO}_3\text{H}$.

Dimethylamine chlorethylsulphonate is difficult to crystallise, and forms an extremely deliquescent mass of silky needles. 20 grams of the salt were acted on with 5 grams of aqueous dimethylamine 33 per cent. solution. The crude dimethyltaurine was dissolved in water, and after evaporating to a syrup, placed in a desiccator. In a few days, a large quantity of fine but indistinct crystals had formed, which after separation from the mother-liquor were redissolved in water and treated as above. In a short time, several large rhombic tables had formed, which were dried by pressing between filter-paper, and submitted to analysis.

- I. 0.4145 gram substance lost 0.0440 gram H_2O over sulphuric acid; at $100\text{--}110^\circ$ the weight did not alter.
 II. 0.2806 gram similarly treated lost 0.0296 gram H_2O .

Calculated for		Found.	
$(\text{CH}_3)_2\text{N.C}_2\text{N}_4\text{SO}_3\text{H} + \text{H}_2\text{O}$		I.	II.
H_2O	10.5	10.6	10.5

III. 0.2168 gram dry substance on combustion with CuO , PbCrO_4 , and Cu gave 0.1448 gram H_2O and 0.2481 gram CO_2 .

IV. 0.3385 gram dry substance after fusion with KHO and KNO_3 produced 0.5220 gram BaSO_4 .

Calculated for		Found.	
$(\text{CH}_3)_2\text{N.C}_2\text{H}_4\text{SO}_3\text{H}$		III.	IV.
C	31.4	31.2	—
H	7.1	7.4	—
S	20.9	—	21.1

Dimethyltaurine is very easily soluble in water, from which it may be crystallised in large rhombic (oblique?) tables containing 1 mol. water, which is completely removed by standing over concentrated sulphuric acid or by dissolving in strong alcohol. It crystallises from the alcoholic solution in snow-like tufts of needles. It is insoluble in ether, and does not deliquesce in air. Dimethyltaurine has a peculiar, not unpleasant taste, which is not at all bitter. It does not melt, but from 270 — 280° becomes dark coloured, and finally decomposes. It has an acid reaction.

Dimethyltaurine forms no combination with hydrochloric acid or platinum tetrachloride. It combines with a molecule of cyanamide, forming dimethyltaurocyamine, which will be described later on.

Diethyltaurine, $\text{NEt}_2\text{C}_2\text{H}_4\text{SO}_3\text{H}$.

The diethylamine salt of chlorethylsulphonic acid forms a gelatinous mass of laminæ, which is very deliquescent. The crude dimethyltaurine could not be crystallised from water, owing to extreme solubility—on standing over sulphuric acid it set to a crystalline mass. This was boiled with absolute alcohol, which dissolved it, and from this solution it was obtained in fine rhombic tables. After three crystallisations, a sample was dried at 100° and analysed:—

- I. 0.1710 gram substance gave 11.8 c.c. moist nitrogen at 15° and 767.7 mm.
- II. 0.2210 gram gave 0.2925 gram BaSO_4 .

Calculated for		Found.	
$(\text{C}_2\text{H}_5)_2\text{N.C}_2\text{H}_4\text{SO}_3\text{H}$		I.	II.
N	7.7	8.0	—
S	17.7	—	18.1

Diethyltaurine, although very easily soluble in water, is not deliquescent. It has a somewhat bitter taste, and melts at 151° . Its reaction is acid.

Methylphenyltaurine, $\text{NMePh.C}_2\text{H}_4.\text{SO}_3\text{H}$.

The methylphenylamine salt of chlorethylsulphonic acid forms a thick syrup with water, and does not appear to crystallise.

Methylphenyltaurine is very difficult to crystallise from water. The syrupy aqueous solution was treated with hot 98 per cent. alcohol, and from this solution it was obtained in silky, indistinct crystals on cooling. A sample which had been twice recrystallised gave the following result on analysis, after drying between filter-paper :—

- I. 0.2410 gram substance gave 13.25 c.c. moist nitrogen at 15° and 767.7 mm.
 II. 0.0913 gram produced 0.1017 gram BaSO_4 .

Calculated for		Found.	
$\text{CH}_3 (\text{C}_6\text{H}_5)\text{N C}_2\text{H}_4.\text{SO}_3\text{H}$.		I	II
N	6.5	6.4	—
S	14.9	—	15.2

Methylphenyltaurine has a very decided acid reaction and taste. Its alcoholic solution becomes violet-coloured. With bleaching powder solution it gives a green, and then a rich blue coloration. Ferric chloride produces no colour until warmed, the liquid then acquires a beautiful green tint.

Trimethyltaurine, $\text{NMe}_2.\text{C}_2\text{H}_4.\text{SO}_3\text{CH}_3$ (?).

The trimethylamine salt of chlorethylsulphonic acid after standing some time over sulphuric acid sets to a compact mass of silky, extremely deliquescent needles.

16 grams of this salt were heated in a sealed tube at 160° for 10 hours, with 20 c.c. of a 25 per cent. solution of trimethylamine in absolute alcohol. On cooling, a quantity of a crystalline substance separated out, which was obviously not the trimethylamine salt. A few preliminary experiments showed that these crystals were insoluble in absolute alcohol, whereas the mother-liquor, which indicated a quantity of chlorine when tested with silver nitrate, was dissolved. The substance insoluble in alcohol contained no chlorine. The whole mass was now digested with absolute alcohol two or three times, until no chlorine could be detected in the alcoholic liquid. The residue was then dissolved in hot water. This solution soon deposited

beautiful crystals, which proved to be pure trimethyltaurine, as the following analyses of the air-dried substance testify.

- I. 0.2006 gram substance on combustion with CuO , PbCrO_4 , and Cu gave 0.1432 gram H_2O , and 0.2628 gram CO_2 .
 II. 0.2920 gram burnt with CuO and copper gauze, with sodium hydrogen carbonate gave 22 c.c. moist nitrogen at 16° and 758.5 mm.

These results worked into percentages agree with the formula for trimethyltaurine:—

	Calculated for $(\text{CH}_3)_2\text{N}.\text{C}_2\text{H}_4.\text{SO}_3\text{CH}_3$.	Found.	
		I.	II.
C	35.9	35.7	—
H	7.8	7.9	—
N	8.4	—	8.6

Trimethyltaurine is easily soluble in water, from which it crystallises in fine rhombic (oblique?) prisms without water of crystallisation. In absolute alcohol and ether, it is insoluble. Strong alcohol precipitates it from its aqueous solution in fine slender tables. It undergoes no change below 300° . It has a sweet, cooling taste, and has a *neutral* reaction. It is decomposed by dilute alkalis, with evolution of trimethylamine. I hope shortly to investigate this reaction carefully, and also to study its action with cyanamide.

Phenyltaurine and Cyanamide. Formation of Phenyltaurocyamine.

Engel has shown that taurine combines with cyanamide, forming a body which he named tauroglycocyamine, from its analogy to glycocyamine (*Ber.*, 8, 1597), and Dittrich, who also prepared this compound without being aware of Engel's work, called it taurocyamine; he also made methyltaurocyamine (*J. pr. Chem.* [2], 18) analogous to sarcosine.

It appeared interesting to ascertain whether phenyltaurine and, say, dimethyltaurine, also united with cyanamide.

Two grams of pure phenyltaurine were dissolved in luke-warm water, and 0.4 gram cyanamide added, the mixture was then heated for five hours at 100 — 110° in a sealed tube. Nothing had crystallised in the tube; on opening it, however, crystals soon began to form, identical in appearance with phenyltaurine. They were washed once or twice with cold water and dried in air. They gave no violet coloration with bleaching powder solution, therefore the substance could not be unaltered phenyltaurine.

On analysis, the following numbers were obtained, which agree with the formula for phenyltaurocyamine:—

- I. 0.1694 gram substance gave 0.0860 gram H_2O and 0.2770 gram CO_2 .
 II. 0.2061 gram gave 30.4 c.c. moist nitrogen at 15° and 767.7 mm.

	Calculated for $\text{C}_6\text{H}_5(\text{CNNH}_2)\text{HN}.\text{C}_2\text{H}_4.\text{SO}_3\text{H}.$	Found.	
		I.	II.
C	44.4	44.6	—
H	5.3	5.6	—
N	17.3	—	17.2

Phenyltaurocyamine crystallises from water in glistening leaves, which contain no water of crystallisation. It has no characteristic taste, and is neutral to litmus. It does not melt at 300° , but becomes brown and decomposes at a somewhat higher temperature.

Dimethyltaurine and Cyanamide. Formation of Dimethyltaurocyamine.

1.5 gram of pure dimethyltaurine was dissolved in water, 0.36 gram cyanamide added, and the mixture heated at 100 — 110° in a closed tube. The liquid, which was perfectly clear, was evaporated to a syrup; on standing for a few days, it set to a semi-solid mass of hard indistinct crystals. These were well pressed between filter-paper, and submitted to analysis with this result:—

- I. 0.5126 gram substance lost 0.0456 gram H_2O , by standing over H_2SO_4 .
 II. 0.1702 gram dry substance on combustion gave 0.1058 gram H_2O and 0.1929 gram CO_2 .
 III. 0.1324 gram dry substance produced 25.2 c.c. moist nitrogen at 16° and 758.5 mm.

H_2O	Calculated for $(\text{CH}_3)_2(\text{CNNH}_2)\text{N}.\text{C}_2\text{H}_4.\text{SO}_3\text{H} + \text{H}_2\text{O}.$	Found.	
	8.45	8.9	

In dry substance :—

		II.	III.
C	30.8	30.9	—
H	6.7	6.9	—
N	21.5	—	21.7

Dimethyltaurocyamine is very easily soluble in water, and insoluble in absolute alcohol and ether. It has a slightly bitter taste. It melts with decomposition at 245° . Its reaction is slightly acid.

General Remarks.

The solubility and melting points of some of the above substances, as well as their reactions with litmus, are worthy of note.

Methyltaurine is insoluble in alcohol: dimethyltaurine is moderately soluble in alcohol, by analogy one would suppose that trimethyltaurine would be more easily dissolved by this liquid; it is, however, insoluble. All three dissolve easily in water.

From the above, it would appear probable that the melting points of these substances would show some anomaly, but this is not the case. Methyltaurine melts at 241° , dimethyltaurine decomposes without melting near 275° , and trimethyltaurine is unaltered at 300° . Mono- and di-substituted taurines have an acid reaction, trimethyltaurine is neutral to litmus.

In no case could salts be obtained from mono- or di-substituted taurines and hydrochloric acid, neither could any crystallised combination with platinum tetrachloride be formed. In these reactions, these derivatives of amido-isethionic acid are sharply distinguished from their carboxyl homologues, amido-acetic and amido-propionic acids.

The yield of crude product is in all cases nearly the theoretical, this also holds for the cyanamide compounds. Dittrich recommends a large excess of methylamine in preparing methyltaurine from the corresponding salt; he says, indeed, that it is absolutely necessary for its formation. I have found, on the contrary, that an excess is altogether unnecessary if the amine salt of β -chloroethylsulphonic acid be employed, the calculated quantity producing nearly the theoretical yield of the substituted taurine. When the silver or lead salt of the acid is used, an excess of amine *is necessary*—a proof that these salts are converted into the amine salts before the final reaction takes place.

XLI.—*A Crystalline Tricupric Sulphate.*

By W. A. SHENSTONE.

A CONSIDERABLE number of basic copper sulphates have from time to time been examined by various chemists. Up to the present, all of them, except bronchantite, native tetracupric sulphate, have been described as amorphous powders of green or orange-yellow colour, which have generally been obtained from the normal sulphate by treatment with cupric oxide or hydrate, or by the action of alkali on

it in quantity insufficient for the production of cupric hydrate. The existence of several of them is doubtful, however, and not long since Pickering (*Chem. News*, 47) stated that only two definite compounds have in reality been prepared in this way. As the salt I am about to describe is a crystalline basic copper sulphate obtained artificially, it is therefore not without interest.

In the course of the experiments on the solubility of salts in water at high temperatures made not long back in conjunction with Dr. W. A. Tilden (*Phil. Trans.*, 1884, Pt. I), I observed in the tubes in which copper sulphate and water had been heated deposits of bright green crystals, always, however, in very small quantity. I was able to prepare rather larger quantities by heating the crystals of copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, at about 200° for a few hours, in tubes containing a few grams of the salt, and draining off the mother-liquor while still hot. By washing the solid part of the contents of the tubes with water a green product consisting of crystalline fragments was obtained. On an average, 0.25 gram per tube was secured.

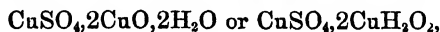
Analysis gave the following results:—

1.	0.2943 gram	gave	0.1913 gram	BaSO_4 .
2.	0.2745	„	0.1811	„ „
3.	0.2384	„	0.1309	„ copper.
4.	0.2459	„	0.1330	„ „

These numbers correspond with the following percentages:—

	SO_4 .	Cu.
1.....	26.78	—
2.....	27.18	—
3.....	—	54.90*
4.....	—	54.08
Mean.....	26.98	—

These results lead to the formula of a tricupric sulphate,



which requires 53.75 per cent. Cu and 27.07 per cent. of SO_4 .

The salt is permanent when heated in the air to 190° , is insoluble in water, soluble in dilute sulphuric acid, and consequently if the substance is left for a few weeks in contact with its mother-liquor, it gradually disappears.

Attempts to prepare other crystalline basic salts by this method have not yet led to any results.

* Known to be high, as the Cu weighed was slightly oxidised in drying it at too high a temperature.

After a great many attempts to obtain large crystals for measurement I have been unable to do so.

Mr. H. A. Miers, of the British Museum, however, very kindly undertook to examine those which I obtained, and his results are given in the supplement to this note. I may say that he tells me it was not possible to get better measurements on account of the small size of the crystals. And that he does not "find any very obvious relation between the forms of the crystals of this tricupric sulphate and those of bronchantite."

XLII.—*Crystallography of $\text{CuSO}_4 \cdot 2\text{CuH}_2\text{O}_2$. (Supplement to XLI.)*

By H. A. MIERS, M.A.

SYSTEM rhombic :—

$$(100) : (010) = 63^\circ 34'. \quad (010) : (011) = 35^\circ 51'. \quad (001) : (101) = 34^\circ 32'.$$

$$a : b : c = 2.0116 : 1 : 1.3842.$$

Forms observed :	$a = \{100\}.$
	$b = \{010\}.$
	$m = \{110\}.$
	$n = \{230\}.$
	$o = \{101\}.$
	$r = \{201\}.$
	$y = \{111\}.$
	$s = \{641\}.$

	Calculated.	Observed.	Limits of variation.
<i>ar</i>	36° 0'	36° 33'	36° 0' to 37° 23'
<i>bm</i>	—	26 26	26 3 „ 26 57
<i>bn</i>	18 20	18 17	—
<i>ao</i>	55 28	54 59	53 48 to 56 36
<i>by</i>	—	41 15	—
<i>mr</i>	68 53	70 46	69 57 to 71 36
<i>or</i>	19 28	18 7	17 22 „ 19 1
<i>ms</i>	12 38	11 12	—

Cleavage *a* imperfect. The faces in the zone *ab* are all striated parallel to their intersections with one another.

The above elements are calculated from the angles *bm* and *by*.

The measurements were made upon seventeen crystals, but these were very minute and imperfect.



All the forms observed are shown in the figure, with the exception of *s*, of which an isolated face was found upon the edge between the faces *mr*.

XLIII.—*A Modified Bunsen Burner.*

By W. A. SHENSTONE.

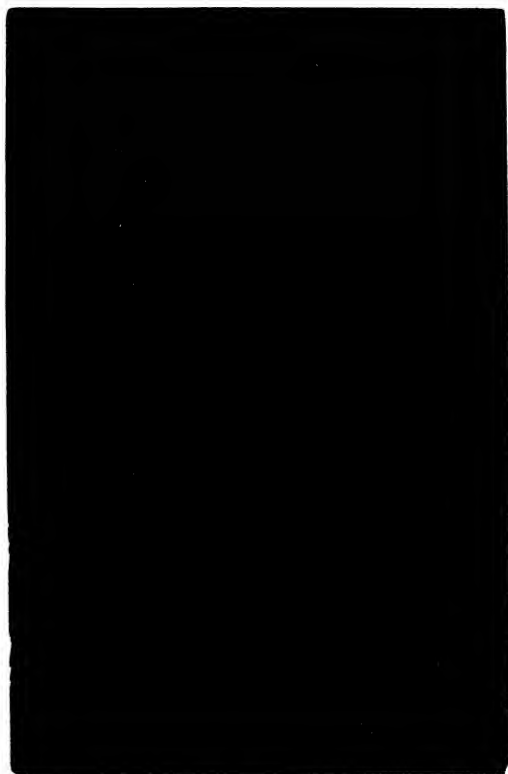
HAVING lately frequently wanted to obtain very accurate results in determining metals, such as calcium, by ignition with sulphuric acid, and having always found all the ordinary methods of avoiding spurting somewhat uncertain when I could not watch the whole process, as frequently happened, I have been led to contrive the burner shown in the accompanying diagram, which enables one to apply heat from above, and so to cause evaporation to take place from the surface of the material in the crucible, and also enable one to regulate the heat applied very easily, and thereby to secure any temperature that is desired.

The diagram is rather under one-fourth of the actual size. It will be found that the crucible shown is rather too large, in proportion to the ring *b*, so that it would be convenient to make the diameter of *b* about half an inch greater than in my arrangement.

The crucible *a* stands on a small atmpyre *c*, which carries a guard of platinum *d* easily made of thin strips of rather thick platinum foil. The ring *b* is pierced with small holes about 1 mm. in diameter, so that a ring of tiny jets of flame or an almost con-

tinuous sheet of flame can be applied to the crucible or other object to be heated. The flame can be applied to the crucible at any convenient level by means of the clamp.

The burner is enlarged, as shown at *e*, and the gas enters at a jet which is fixed just below the point *f* where the narrow part of the burner is attached to the air-chamber. It is necessary to adjust the position of the gas-jet with some care at starting, in order to secure a non-luminous flame. The large air-chamber *e* appears to be necessary, in order to obtain complete combustion.



It will be seen that only the ring burner need be specially provided for setting up this contrivance, as ordinary clamps and stands and clay atpomyres can be employed.

With a little attention on the first occasion of its use, I have found that it answers its purpose admirably, and as I have not seen any such burner described as far as I remember, I have thought it useful enough to be worth this notice.

XLIV.—*On some Points in the Composition of Soils; with Results Illustrating the Sources of the Fertility of Manitoba Prairie Soils.**

By Sir J. B. LAWES, Bart., LL.D., F.R.S., F.C.S., and J. H. GILBERT, Ph.D., LL.D., F.R.S., V.P.C.S.

THIS paper may be considered as a continuation of one read in the Chemical Section, at the meeting of the American Association for the Advancement of Science held at Montreal, in August, 1882, entitled—"Determinations of Nitrogen in the Soils of some of the Experimental Fields at Rothamsted, and the Bearing of the Results on the Question of the Sources of the Nitrogen of our Crops,"—and in order adequately to bring out the bearings of the new results, embodied in the present communication, it is desirable, first to summarise the main results and conclusions of the previous one.

The question of the sources of the nitrogen of our crops is one respecting which very conflicting views are still entertained; and it may at once be admitted that so long as the facts of agricultural production alone are studied, without knowledge of, or reference to, the changes in the stock of nitrogen in the soil, it would seem not unreasonable to assume that a large proportion of the nitrogen, at any rate of some crops, must be derived, in some way or other, from the atmosphere.

Yield of Nitrogen per Acre in Different Crops.

Obviously, it is a point of first importance to determine what really is the annual yield of nitrogen in different crops over a given area, excluding, as far as possible, the amounts due to unknown supplies by manure; thus, as far as practicable, limiting the source to the stores of the soil itself, and to the atmosphere. The Rothamsted field experiments, in which different crops have been grown for very many years in succession on the same land, both without nitrogenous manure, and with known quantities of such manure, afford valuable data of the kind required; and, in our former paper, the results were discussed in some detail. It must suffice here to summarise them very briefly.

The average yield of nitrogen per acre per annum was, in wheat, 32 years without manure 20·7 lbs., and 24 years with a complex

* Read before the Chemical Section, at the Montreal Meeting of the British Association for the Advancement of Science, September 2, 1884.

mineral manure 22·1 lbs. ; in barley, 24 years without manure 18·3 lbs., and 24 years with a complex mineral manure 22·4 lbs. ; in root-crops, 36 years (including 3 of barley), with a complex mineral manure 25·2 lbs. ; in beans, 24 years without manure 31·3 lbs., and 24 years with a complex mineral manure 45·5 lbs. ; in clover, 6 crops in 22 years, with 1 of wheat, 3 of barley, and 12 years of fallow, without manure 30·5 lbs., and with a complex mineral manure 39·8 lbs. ; in clover on land which had not grown the crop for many years, 1 year 151·3 lbs. ; in a rotation of crops, 7 courses, 28 years, without manure 36·8 lbs., and with superphosphate of lime 45·2 lbs. ; in the mixed herbage of grass land, 20 years without manure 33 lbs., and with complex mineral manure, including potass, 55·6 lbs. ; lastly, with Bokhara clover, 5 years, with mineral manure, 92 lbs. of nitrogen, per acre per annum.

Thus, the annual yield of nitrogen per acre, none being supplied in manure, was the least in the cereal crops, more in the root-crops, and much more still in the leguminous crops, whilst in a rotation of crops, in which roots and Leguminosæ were interpolated with cereals, the annual yield of nitrogen was very much greater than in cereals grown year after year on the same land.

But, an essential point to remark is, that in all the experiments on arable land, whether with cereal crops, root-crops, leguminous crops, or a rotation of crops, grown without nitrogenous manure, *the decline in the annual yield of nitrogen was very great* ; and this was the case even when a full mineral manure was applied. Even with the deep-rooted *Melilotus leucantha* the crops of the sixth and seventh years show a considerable decline in yield.

The Sources of the Nitrogen of Crops.

The next question is—what are the possible sources, other than the soil itself, of the amounts of nitrogen annually yielded in crops over a given area, when none is supplied by manure ? This part of the subject was considered in some detail in our former paper, as it has been on previous occasions. It is only necessary here to state very briefly the general results of these former inquiries.

1. Combined Nitrogen in Rain, &c.

In Liebig's earlier writings, he assumed the probability of a very much larger quantity of ammonia coming down in rain than he did subsequently, but even in his *Natural Laws of Husbandry*, published in 1863, he concluded that as much as 24 lbs. of nitrogen per acre may be annually available to vegetation from that source. It is obvious that such an amount would do much towards meeting the requirements of many of the crops the yield of nitrogen in which has been given above.

In 1852, Boussingault determined the amounts of ammonia in the rain collected in Alsace during a period of nearly six months. His average amount of ammonia per million of rain was somewhat less than that found at Rothamsted in 1853, 4, 5, and 6; with approximately the same annual rainfall in the two localities. The amount of combined nitrogen found in the Rothamsted rain at that time corresponded to a deposit of about 6 lbs. as ammonia, and about $\frac{3}{4}$ lb. as nitric acid, per acre per annum; or in all less than 7 lbs.; whilst more recent determinations made at Rothamsted lead to the conclusion that the total amount of combined nitrogen contributed in the rain and the minor measured aqueous deposits probably does not exceed 5 lbs. per acre per annum; including that as ammonia, as nitric acid, and in organic matter.

Determinations of ammonia and nitric acid in the rain of numerous localities on the continent of Europe have been made, and the mean result for nine places, some urban and some country, and representing in all the collection of 22 yearly periods, corresponds to an average annual supply of about $10\frac{1}{4}$ lbs. of combined nitrogen per acre per annum.

Upon the whole, therefore, we are disposed to conclude that the supply of combined nitrogen coming down in the measured aqueous deposits from the atmosphere, little, if at all, exceeds 5 lbs. per acre per annum, in the open country, in Western Europe.

With records of the amounts contributed in rain and the minor aqueous deposits, we come to an end of all quantitative evidence as to the amounts of combined nitrogen available to the vegetation of a given area from atmospheric sources; and it will be seen that the amount so available is very far from adequate to supply the quantities annually yielded in different crops grown without nitrogenous manure.

It is true that the minor aqueous deposits from the atmosphere are much richer in combined nitrogen than rain; and there can be no doubt that there would be more deposited within the pores of a given area of soil than on an equal area of the non-porous even surface of a rain-gauge. There is, however, no evidence enabling us to estimate how much may be available from this source, in addition to that determined in the collected aqueous deposits. The quantity will doubtless vary according to the character, and to the temporary mechanical condition, of the soil; and the quantity absorbed and retained may be influenced by the character of the vegetation with which the land is covered. Still, such as it is, the evidence at command bearing on the point, leads to the conclusion that the amounts so available are but small, and quite inadequate to make up the deficiency between the amounts supplied directly in rain, and those yielded in the crops grown without nitrogenous manure.

Other Supposed Sources of Combined Nitrogen.

Among other possible supplies of combined nitrogen to the soil from atmospheric sources, it has been supposed that, in the last stages of the decomposition of organic matter in the soil, hydrogen is evolved, and that this nascent hydrogen combines with the free nitrogen of the atmosphere, and so forms ammonia; or that in the oxidation of organic matter in the soil, there may be an evolution of ozone, which, combining with free nitrogen, forms nitric acid.

We have on former occasions given reasons for concluding that these supposed sources cannot be taken as accounting for the facts of growth. Indeed, such evidence as exists on the point, even supposing these actions take place at all, leads to the conclusion that any amounts of combined nitrogen so available must, like those due to direct condensation by the porous soil, be both limited and inadequate.

But if the supplies from the atmosphere to the soil are inadequate, may not there be direct supply from the atmosphere to the plant itself?

Here again, the conclusion arrived at, after careful consideration of the evidence available was, that even broad-leaved plants, such as the root-crops for example, which have been assumed to absorb a considerable quantity of ammonia from the atmosphere by their leaves, do not derive any material amount of their nitrogen in that way.

Lastly, comes the question whether plants assimilate the free nitrogen of the atmosphere, and whether some descriptions do so in a much greater degree than others.

On this point there is a great deal of experimental evidence at command; but the results are very conflicting, and we have concluded that the balance of the evidence is decidedly against the supposition that plants do assimilate the free nitrogen of the atmosphere.

To recapitulate: the amounts of combined nitrogen annually coming down in the measured aqueous deposits from the atmosphere in the open country are quite inadequate to supply more than a small proportion of the nitrogen assimilated by crops over a given area, when none is supplied by manure. With regard to other possible supplies of combined nitrogen to the soil, there is no direct quantitative evidence at command, but such evidence as does exist points to the conclusion that such supplies are at any rate very limited and inadequate. The same may be said of the supposed combination of the free nitrogen of the air within the soil; also of the supposition that plants take up any material proportion of their nitrogen from combined nitrogen in the atmosphere by their leaves. Finally, the balance

of direct experimental evidence is against the supposition that plants assimilate the free nitrogen of the atmosphere.

The Nitrogen of the Soil as a Source of the Nitrogen of Crops.

The special object of our former paper, as indicated by its title, was to record and discuss determinations of nitrogen in the soils of some of the experimental fields at Rothamsted, and to show the bearing of the results on the question of the sources of the nitrogen of the crops grown.

When it is borne in mind that a difference in the amount of nitrogen in the soil of 0.001 per cent. may represent a difference of 20 to 25 lbs. per acre in a layer 9 inches deep, it will be seen how difficult it is to obtain results which are applicable for estimating the loss or gain of the soil from one period to another. In our former paper, these difficulties were considered in some detail, and the methods of collecting and preparing samples of soils for analysis were described.

Further, it was concluded that, owing to the low actual percentage of nitrogen in subsoils, and to the proportionally great variation in the percentage in different samples taken from the same plot and to the same depth, obviously due to natural inequalities, and unconnected with the special history of the plot, it was in most cases misleading to attempt to estimate changes in the stock of the total nitrogen of the soil beyond a comparatively limited depth from the surface—in fact very little beyond the depth to which the soil is influenced by the mechanical operations in the case of arable land, and by active root-development in that of grass land. Accordingly, most of our calculations of *total nitrogen* in the soil have been limited to that in the first 9 inches of depth.

Although the results of the determination of *total nitrogen* in the subsoils of different plots are thus inapplicable for the calculation of the loss or gain of the soil to any considerable depth, yet the determinations of the amounts of nitrogen existing as nitric acid—that is, of nitrogen in a soluble, and, so to speak, migratory condition—in the subsoils of plots in different conditions, induced by cropping or manuring, have much significance. It is a special object of the present paper to bring forward the results of new determinations of nitrogen as nitric acid, in soils and subsoils of known history, in some cases to the depth of twelve times 9 inches, or in all to 108 inches.

In order that the bearing of these new results on the question of the sources of the nitrogen of our crops may be better understood, it is desirable first to summarise the results and conclusions of our

former paper, both as to the amount of total nitrogen, and the amounts of nitrogen as nitric acid, found in various soils.

The Experimental Wheat-field Soils.—In the case of the field in which wheat has now been grown year after year from 1844 up to the present time, samples of the soils of many of the plots were taken in 1865, after 22 crops had been removed, and again in 1881, when 16 more had been taken. In these samples, the nitrogen was determined by the soda-lime method, and in some of them the nitrogen as nitric acid also.

It has been stated that on the continuous wheat-plot without any manure, and on that with mineral, but without nitrogenous manure, there was a marked decline in the annual yield of nitrogen per acre in the crops. The determinations of nitrogen in the soils showed that, with this decline of yield in the crops, there was also a marked reduction in the stock of nitrogen in the soils.

Calculation further indicated that the soil had lost nitrogen in amount corresponding to about two-thirds the quantity removed in the crops and lost by drainage. The conclusion was, that the soil itself had contributed, at any rate the greater part of the nitrogen annually removed in the crop and lost by drainage. The combined nitrogen in the rain and minor aqueous deposits, together with that in the seed sown, would supply most of the remainder. Thus there was very little to be provided from all the other possible sources taken together.

The Experimental Barley-field Soils.—From some of the plots in the field which has grown barley every year from 1852 up to the present time, samples of soil were taken in 1868, and again in 1882. Between these dates 13 barley crops had been removed. On the plot which had received a complex mineral manure every year, but no nitrogen, the records of average annual yield of nitrogen in the crops showed a gradual decline over the later years; and the nitrogen determinations in the soils showed, as in the case of the wheat soils, a reduction in the stock of nitrogen in the first 9 inches of depth.

The Experimental Root-crop Soils.—With the exception of 3 years (1853, 4 and 5), when barley was taken without manure, roots have been grown on the same land from 1843 up to the present time. Samples of the soil were taken in 1870 only; but then from 35 different plots. Having only taken samples once, the condition of the land at different periods cannot be compared. But, in the case of 4 plots, one entirely unmanured, and 3 with purely mineral manure, every year, the percentage of nitrogen in the first 9 inches of depth was at that time, that is, after 27 years of experiment, found to be lower than in any other of the experimental fields; though deter-

minations made in samples from other parts of the same field, and also from an adjoining field, show much higher results.

Now, the yield of nitrogen in the root-crops was, in the earlier years, much higher than, and in the later as low as, in the case of the cereals; and it is quite consistent with the conditions of soil known to be favourable for the growth of root-crops, and with the amount of fibrous root they throw out near the surface, that their growth should lead to a greater reduction in the stores of nitrogen of the superficial layers than in the case of other crops. In fact, the conclusion is, that the dependence of root-crops for their nitrogen on the stores of the soil itself, or on supplies by manure, is as clearly established as in the case of the cereals.

The Nitrogen of the Leguminosæ.

It has been shown that the leguminous crops yield much more nitrogen per acre than either cereals or root-crops, but that when grown continuously without nitrogenous manure, they, like the other crops, decline in annual yield.

The Experimental Bean-field Soils.—These experiments were commenced in 1847, and continued with some breaks until 1878. Without manure, the yield of nitrogen was in the earlier years much higher than in the cereals; but it declined very much, and in the later years it was as low as in the cereals. With mixed mineral manure, including potash, the yield was throughout much higher, but still the decline was very great. In 1857, and in 1865, samples of the soils of some of the plots were taken, and in 1883 of a greater number. Confining attention to the unmanured and mineral manured plots, that is to the plots to which no nitrogenous manure has been supplied, the soils show a very distinct reduction in total nitrogen in the first 9 inches of soil.

The Experimental Clover-land Soils.—An attempt was made to grow clover many years in succession on the same land, the experiment commencing in 1849, and ending in 1877, that is, extending over a period of 29 years. In the early years, some good crops were obtained, and small cuttings at intervals afterwards; but the plant very frequently died off in the winter and spring succeeding the sowing of the seed, so that only 8 years have yielded clover. In 1 year wheat, and in 5 barley, was taken; and in 12 years the land remained fallow.

Notwithstanding that so few crops of clover were produced, that 6 grain crops were grown, and that the land was many years practically fallow, the effect of the interpolation of the clover was to increase the average annual removal of nitrogen from the land considerably beyond that obtained in cereals grown continuously.

In 1881, samples were taken from the clover plots in 5 places, where no nitrogen had been applied; and determinations of nitrogen in them showed nearly as low a percentage in the first 9 inches of depth, as in the soil of an adjoining plot which had been 30 years under alternate wheat and fallow without any manure, and as in the soil of the exhausted root-crop land.

It is significant that, after good crops of clover in the early years, when the land was in ordinary condition, but constant failure afterwards, the percentage of nitrogen in the surface soil should be nearly as low as with alternate wheat and fallow without manure.

In an immediately adjoining field, after 6 grain crops had been grown in succession by artificial manure, the land was divided, and, in 1873, on one half clover (sown in the spring of the previous year), and on the other half barley, was grown. In the clover crops 151·3 lbs., and in the barley only 37·3 lbs. of nitrogen were removed; yet, in the next year (1874), barley being grown on both portions, the one from which 151·3 lbs. of nitrogen had been removed in clover yielded 69·4 lbs. in barley, whilst the one from which only 37·3 lbs. had been removed in the barley yielded only 39·1 lbs. in barley again.

In October, 1873, after the clover and barley had been removed, samples of soil were taken from 10 places on each portion; and determinations showed that there was a considerably higher percentage of nitrogen in the first 9 inches of the clover land than to the same depth of the barley land. This result, and the increased crop of barley succeeding the clover, are quite consistent with what is known of the influence of a clover crop as a preparation for a succeeding cereal one. But the actual amount of gain of nitrogen indicated in the surface soil was greater than the amount removed in the clover crops, which it seems difficult to suppose would be the case; though comparative samples were again taken 4 years later, and these also showed a higher percentage in the clover soil.

It is obvious that the clover, and the surface soil of the clover ground, had gained nitrogen either from the atmosphere or the sub-soil; nor do the facts of the experiment afford evidence of the source of the nitrogen. There is, however, nothing in favour of the view that the atmosphere is the source, excepting that an explanation is needed; whilst it will be seen further on that there is direct evidence that the nitrogen of the soil is at any rate the source of much of the nitrogen of the Leguminosæ.

In view of the signal failure of clover on the nitrogen-exhausted arable soil, it is of much interest that large, but still declining crops, have been grown on a small plot of rich kitchen-garden ground for 31 years in succession.

The experiment was commenced in 1854. Samples of soil were taken in October, 1857, and in May, 1879, that is, with an interval of 21 seasons of growth. In 1857, only one sample was taken, and only to the depth of 9 inches; but in 1879 three were taken, in each case to the depth of twice 9, or 18 inches.

In 1857, the first 9 inches of soil showed more than 0·5 per cent. of nitrogen, or nearly 5 times as much as the exhausted arable soil in which clover would not grow. It is true the garden soil would also be rich in all other constituents; but some portions of the arable soil where the clover failed had received much more of mineral constituents by manure than had been removed in the crops.

The determinations of nitrogen made in the three 1879 samples of soil agreed very well, and they showed a reduction of 29 per cent. of the total nitrogen of the first 9 inches of soil since 1857. The reduction corresponded to a loss of 2732 lbs. per acre in the first 9 inches of depth during the 21 years; and it is to be remarked that with this great reduction in the stock of nitrogen in the soil there has also been a great falling off in the clover-growing capability of the soil, though mineral manures have from time to time been applied to a portion of the plot.

As nearly as can be estimated, the yield of nitrogen in the clover crops corresponded to about 200 lbs. per acre per annum over the 21 years; whilst the estimated loss of nitrogen by the first 9 inches of soil is about 130 lbs. per acre per annum; corresponding approximately to two-thirds of the amount removed in the crops. There is, however, reason to suppose that in the case of soils to which excessive amounts of farmyard manure are applied, there may be a loss by the evolution of free nitrogen, and so far as this may have occurred in this garden soil, there will be the less of the loss to be credited to the growing clover. On the other hand, in 1879, that is, at the end of the period under consideration, the second 9 inches of depth showed about three times as high a percentage as the subsoils of the arable fields, and even nearly twice as high a percentage as the surface soil of the field where the clover had so frequently failed. It cannot be doubted, therefore, that the subsoil of the garden plot had contributed to the yield of nitrogen in the clover.

There is, in fact, in the results of this experiment on a rich garden soil, if not absolute proof, certainly very strong ground for concluding, that much, and perhaps the whole, of the nitrogen of the 30 years of luxuriant clover crops was derived from the stores of nitrogen of the soil itself—supplemented only by the small amount of combined nitrogen annually coming down in the measurable aqueous deposits, and that condensed within the pores of the soil.

The Experimental Mixed Herbage Soils.—Over a period of 20

years, the mixed herbage of permanent grass land yielded an average of 33 lbs. of nitrogen per acre per annum without manure, and 55·6 lbs. with a mixed mineral manure, containing potash, but no nitrogen. Whence comes the increased amount of 22·6 lbs., under the influence of the purely mineral manure? In 1870, that is after 20 crops had been removed, samples of the soils were taken, and the nitrogen determined in them. Calculated per acre, the results indicated that the first 9 inches of depth of the mineral-manured plot contained, at the end of the 20 years, 506 lbs. less nitrogen than the unmanured plot to the same depth; corresponding to an annual reduction of 25·3 lbs. of nitrogen, against 22·6 lbs. per acre per annum more yielded in the crop. The coincidence is very remarkable; and the result can certainly leave little doubt that the increased amount of nitrogen in the crops had its source mainly, if not exclusively, in the surface soil.

In the case of the large crops of clover growing on the ordinary arable soil, it was assumed that, so far as the nitrogen was derived from the soil, it was mainly from the subsoil; but in the case of the clover on the rich garden soil it was concluded that it came largely from the upper layers; and here again, in the case of the mixed herbage, it is supposed that the increased yield is derived from the surface soil. In the first place, the surface soil of the garden ground was about four times, and that of the grass-land about twice as rich as that of the arable land. Further, it is known that clover growing on ordinary arable soil throws out much deep root. Then, again, although in the case of the mixed herbage experiment there was a considerable increase in the amount of leguminous herbage under the influence of the mineral (potash) manure, it was chiefly of the *Lathyrus pratensis*, which throws out a very large amount of root near the surface. There was also, in the later years, a considerable increase in the amount of gramineous herbage, more than would be expected under the direct influence of mineral manures, judging from their effects on the cereals on ordinary arable land. But, in the mixed herbage experiment the increase of the grasses did not take place at all prominently until after an increased growth of Leguminosæ; the surface soil of the grass land was about twice as rich in nitrogen as ordinary arable soil; and the grasses developed were characteristically surface-rooting species.

The Melilotus leucantha, and Trifolium repens, Soils.—On the arable soil on which red clover had, for many years, entirely failed to grow, and the percentage of nitrogen in the surface soil had been reduced to a very low point, the deep-rooted *Melilotus* grew very luxuriantly for several years. The seventh crop in succession has now been taken. The heaviest crop was obtained in the fifth year, 1882; its contents of

nitrogen was between 140 and 150 lbs. per acre; and the average yield over the five years was about 92 lbs. In the sixth and seventh years the produce has been less; and less than on a second plot on which the same plant was grown for the first time in the sixth year. This result is indication that the growth is failing on the original plot. Still, the average yield of nitrogen per acre in this strong and deep-rooted plant, on soil where the much less powerful, yet still deep rooted red clover had entirely failed for many years, was over the 7 years between 70 and 80 lbs. per annum; whilst, side by side with it, both red and white clover, growing under exactly similar conditions of soil and season, yielded scarcely any produce at all.

After the removal of the very heavy crop of *Melilotus* in the fifth year, 1882, samples of soil were taken from the *Melilotus* and the white clover plots, to the depth of 6 times 9, or 54 inches.

For reasons already stated, the determinations of total nitrogen in subsoils are not applicable for calculations of the comparative condition of the two plots in that respect. But the following facts are of much significance. Determinations of moisture in the soils and subsoils, at each of the six depths, showed much less water remaining in the *Melilotus* than in the white clover soils; and the difference was by far the greater at the lower depths. Calculated per acre, it would appear that the *Melilotus* soil had lost to the depth of 54 inches, 540 tons more water than the white clover soil, and the action had doubtless extended lower still.

Thus the plant whose habit of growth, and especially whose range, and feeding capacity, of root, enabled it to take up much more water, and doubtless much more food, from the subsoil than the plant of weaker habit and more restricted root-development, assimilated a much larger amount of nitrogen over a given area, and a legitimate inference is that it had, in some way, derived more nitrogen, as well as water and other constituents, from the subsoil. Further evidence will be given on this point.

Nitrogen as Nitric Acid in Various Soils and Subsoils.

We now come to the consideration of evidence of another kind bearing upon the question of the soil-source of the nitrogen of our crops. It is in reference to this part of the subject that we have new and important results to communicate, but it will be desirable first to refer briefly to those which have already been published.

In the first place it should be stated that the water passing through three drain-gauges, containing respectively 20, 40, and 60 inches depth of unmanured and uncropped soil, and exposed to receive the rainfall, contained, taking the average of several consecutive years,

nitrogen as nitric acid corresponding to about 40 lbs. of nitrogen per acre per annum. Of this, perhaps not much more than 5 lbs., and pretty certainly less than 10 lbs., would be due to combined nitrogen in rain, and condensed by the soil from the atmosphere. There would thus be from 30 to 35 lbs. annually due to the nitrification of the nitrogenous matter of these unmanured soils.

The following Table (p. 392), shows the amounts of nitrogen as nitric acid, found to specified depths, in soils under known, and for the most part strictly comparable, conditions.

In the first experiment, the land had been under rotation for many years, with no other manure than superphosphate applied every fourth year; that is for the root-crop commencing each course of—roots, barley, beans or fallow, and wheat. The samples of soil were taken from parallel plots, the difference between the two being that one had grown beans, and the other had been fallow. It will be seen that, down to the depth of 18 inches, the bean-soil contained 25·8 lbs. less nitrogen as nitric acid than the fallow soil.

In the second experiment, the land received both mineral and nitrogenous manure at the commencement of each rotation, and here, three years after the manuring, there was more nitrogen as nitric acid found, to the depth of 18 inches, than on the superphosphate plot; but 28·3 lbs. less after the growth of beans than after fallow.

In the third experiment, the manuring was the same as in the second, the samples were taken at the same period of the rotation, four years later, and to the depth of 27 inches, instead of only 18. Here there were 40·3 lbs. less nitrogen as nitric acid, to 27 inches of depth, after clover than after fallow.

In these three experiments, there is pretty clear evidence that the leguminous crops, beans and clover, had taken up nitrogen as nitric acid from the soil.

The fourth experiment has reference to land which had been alternately in wheat and fallow, without any manure, for nearly 30 years. The samples of soil taken after the removal of the wheat show very little nitrogen as nitric acid in the first 9 inches of depth, and only traces in the second 9 inches; and to the depth of 18 inches there were 31·1 lbs. less than in the land that had been left fallow. It is seen how completely the wheat had exhausted the upper layers of the soil of their nitric acid.

The fifth and sixth divisions of the Table show the amounts of nitrogen as nitric acid found in the autumn, to the depth of 27 inches, in soils under ordinary conditions as to manuring and cultivation, after having been left fallow since the harvest of the previous year. The quantities still remaining within that depth correspond to not much less than 60 lbs. per acre.

TABLE I.

Nitrogen as Nitric Acid, in various Soils at Rothamsted.

Previous cropping and manuring.	Nitrogen as nitric acid, per acre, lbs.			
	First 9 inches.	Second 9 inches.	Third 9 inches.	Total.
<i>Rotation (Superphosphate); Agdell Field, Sept. 1878.</i>				
Fallow	22·3	14 0	—	36·3
Beans	7·2	3·3	—	10 5
Difference....	15·1	10 7	—	25·8
<i>Rotation (Full Manure); Agdell Field, Sept. 1878.</i>				
Fallow	30·0	18·8	—	48·8
Beans	12 1	8·4	—	20·5
Difference....	17 9	10 4	—	28·3
<i>Rotation (Full Manure); Agdell Field, Sept. 1882.</i>				
Fallow	40·1	14·3	5·5	59·9
Clover	11 4	4·8	3·4	19 6
Difference....	28·7	9·5	2·1	40 3
<i>Wheat and Fallow (Unmanured); Hoosfield, Sept. 1878.</i>				
Fallow	28 5	5·2	—	33·7
Wheat	2·6	trace	—	2 6
Difference....	25·9	5·2	—	31·1
<i>Ordinary Cultivation; Claycroft Field, Oct. 1881.</i>				
Fallow.....	16·4	26 5	15 9	58·8
<i>Ordinary Cultivation; Foster's Field, Oct. 1881.</i>				
Fallow.....	14·6	24·6	17·3	56·5

Lastly, in the experiment in which various leguminous plants were grown on the land on which red clover had so persistently failed, samples of soil were taken to the depth of 6 times 9 inches after the removal of the very heavy crop of *Melilotus leucantha*, and of the very meagre crop of white clover, in 1882. At each depth, the *Melilotus* soil contained less nitrogen as nitric acid than the white clover soil. It will be remembered that the *Melilotus* subsoil had lost very much more water than the white clover soil; and, excluding the first 9 inches of depth, the reduction in the nitrogen as nitric acid was greater at the lower depths. In all, to the six depths, the *Melilotus* soil contained 17·8 lbs. less nitric nitrogen than the white clover soil.

There is here pretty direct evidence that the nitrogen as nitric acid within the soil has been the source of at any rate some of the increased nitrogen of the *Melilotus*; though the quantity indicated is quite inadequate to account for the large amount of the increased yield. But the formation and the distribution of nitric acid within the soil are so dependent on the temporary conditions of temperature, moisture, and growth, that it is not to be expected that the amount found at any one time should account for the requirements of growth. Then, the action would doubtless extend deeper than is represented by the samples taken. It was suggested in the former paper that, with the strong and deeply distributing roots, the drawing up of water, and the greater disintegration and aëration accordingly, nitrification would probably be favoured in the lower layers, and that, if so, the supply would in a sense be cumulative. It was also suggested whether some of the nitrogen of the plant might not be taken up from the subsoil in other forms than that of nitric acid. These points will be further elucidated in the course of the discussion of the new results.

THE NEW RESULTS.

Nitrogen as Nitric Acid in Various Experimental Soils and Subsoils at Rothamsted.

We now come to the consideration of new determinations of nitrogen as nitric acid in various soils and subsoils. The determinations of nitric acid were made by Mr. D. A. Louis, by Schlösing's method, as nitric oxide, by the reaction with ferrous salts.

Towards the end of July, 1883, after the removal of the crops, samples of soil were taken, not this time from the *Melilotus* plot, but from two *Vicia sativa* plots, and from one *Trifolium repens* plot, in each case to the depth of 12 times 9 inches, or in all to the depth of 108 inches. Both the *Vicia sativa* plots gave fairly luxuriant crops, but there was no plant at all on the white clover plot. Samples of soil were also taken at the same time, and to the same depths, from

the immediately adjoining unmanured alternate wheat and fallow land, from the portion which had been fallow since the harvest of the previous year.

The following table (p. 395) shows the amounts of nitrogen as nitric acid, calculated per acre, at each depth in the wheat-fallow land, in the *Trifolium repens* plot, and in each of the *Vicia sativa* plots. It also shows the amounts, at each depth, more or less in the leguminous plot soils than in the wheat-fallow soil; and the amounts more or less in the *Vicia sativa* soils which yielded good crops, than in the *Trifolium repens* soil which gave no crop.

In the case of the wheat-fallow land, samples were taken at four places; and the figures given in the table are calculated from the results of determinations made in a mixture of the soils from the four holes, for each corresponding depth. In the case of each of the leguminous crop plots, samples were taken at two places; and, as in the case of the wheat-fallow plot, determinations of nitric acid were first made in a mixture of the samples from the two holes for each depth, but afterwards in the sample from each separate hole; and the results given for each depth are calculated from the mean of, first, the average of the determinations made in the samples from the individual holes, and, secondly, of the determinations made in the mixture from the two holes. Considerable differences were, in some cases, found in the amount of nitrogen as nitric acid in the separate samples from the same plot at corresponding depths; and these were found to be associated with great differences in the character of the subsoils, as to the proportions of clay, gravel, sand, &c., and with these, differences in the amounts of water, total nitrogen, &c. But whether the results for the individual holes, or for the two, be adopted, there is the same characteristic difference between plot and plot, as to their contents of nitrogen as nitric acid; that is to say, it is always very decidedly in the same direction, differing only more or less as to amount.

The first point of comparison that it is important to call attention to is the very marked difference between the amounts of nitrogen as nitric acid in the wheat-fallow land and in the *Trifolium repens* land.

At each depth, from the first to the twelfth, that is down to 108 inches in all, the *Trifolium repens* land contains much more nitrogen as nitric acid than the wheat-fallow land.

The two plots are absolutely adjoining in the same field. The one plot has been alternately wheat and fallow, without any manure, since 1850, or for more than 30 years. The other was sown with red clover 12 times during the 30 years 1848—1877; in 8 out of the last 10 trials, the plant died off in the winter or spring succeeding the

TABLE II.

Nitrogen as Nitric Acid, per acre, lbs., in the Soils of some Experimental Plots, without Nitrogenous Manure for more than 30 years.

Hoosfield, Rothamsted. Samples Collected July 17-26, 1883.

Depths.	Wheat-fallow land, unmanured.	Series 1. Mineral manures.			+ or - wheat land.			+ or - Trifolium repens.	
		Trifolium repens. Plot 4.	Vicia sativa. Plot 4.	Vicia sativa. Plot 6.	Trifolium repens. Plot 4.	Vicia sativa. Plot 4.	Vicia sativa. Plot 6.	Vicia sativa. Plot 4.	Vicia sativa. Plot 6.
inches.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
1-9	19·85	30·90	12·16	10·22	+ 11·05	-7·69	-9·63	-18·74	-20·68
10-18	8·05	27·73	4·11	2·72	+ 19·68	-3·94	-5·33	-23·62	-25·01
19-27	2·47*	8·44	1·37	1·08	+ 5·97	-1·10	-1·39	-7·07	-7·36
28-36	2·70	7·64	1·67	1·52	+ 4·94	-1·03	-1·18	-5·97	-6·12
37-45	1·62	9·07	4·58	2·51	+ 7·45	+ 2·96	+ 0·89	-4·49	-6·56
46-54	3·57	8·77	6·37	4·42	+ 5·20	+ 2·80	+ 0·85	-2·40	-4·35
55-63	3·84	7·92	7·16	4·52	+ 4·08	+ 3·32	+ 0·68	-0·76	-3·40
64-72	2·28	8·34	5·95	4·92	+ 6·06	+ 3·67	+ 2·64	-2·39	-3·42
73-81	1·48	8·27	4·54	4·81	+ 6·79	+ 3·06	+ 3·33	-3·73	-3·46
82-90	1·76	9·95	5·32	5·14	+ 8·19	+ 3·56	+ 3·38	-4·63	-4·81
91-99	2·94	9·16	5·66	6·40	+ 6·22	+ 2·72	+ 3·46	-3·50	-2·76
100-108	1·84	9·51	5·32	6·46	+ 7·67	+ 3·48	+ 4·62	-4·19	-3·05

Summary.

1-27	30·37	67·07	17·64	14·02	+ 36·70	-12·73	-16·35	-49·43	-53·05
28-54	7·89	25·48	12·62	8·45	+ 17·59	+ 4·73	+ 0·56	-12·86	-17·03
55-81	7·60	24·53	17·65	14·25	+ 16·93	+ 10·05	+ 6·65	-6·88	-10·28
82-108	6·54	28·62	16·30	18·00	+ 22·08	+ 9·76	+ 11·46	-12·32	-10·62
1-54	38·26	92·55	30·26	22·47	+ 54·29	-8·00	-15·79	-62·29	-70·08
55-108	14·14	53·15	33·95	32·25	+ 39·01	+ 19·81	+ 18·11	-19·20	-20·90
1-18	27·90	58·63	16·27	12·94	+ 30·73	-11·63	-14·96	-42·36	-45·69
19-108	24·50	87·07	47·94	41·78	+ 62·57	+ 23·44	+ 17·28	-39·13	-45·29
1-108	52·40	145·70	64·21	54·72	+ 93·30	+ 11·81	+ 2·32	-81·49	-90·26

* According to the determinations on the mixture from the four holes, the result was 10·24 lbs., but this being obviously too high, determinations were made in the samples from each of the four holes separately, when the amount indicated in the third was found to be so abnormally high (=25·9 lbs.) as to leave no doubt that there had been accidental contamination of the sample, and the results for the three other holes have accordingly been adopted.

sowing of the seed, in 4 of these without giving any crop, and in the other four only very small cuttings; and during the 30 years, consequent on the failure of the clover, 1 crop of wheat and 5 of barley have been taken, and the land was 12 years fallow. White clover (*Trifolium repens*) was then sown in 1878, 1880, 1881, and 1883. A small cutting was obtained in 1879, very small ones were taken in 1880 and 1881, and a small one in 1882, but none in 1883, so that the land was practically fallow when sampled. The plot had not received any nitrogenous manure for about 35 years. This and the other leguminous plant plots had, however, from time to time received mineral manures, containing phosphoric acid and potash, whilst the wheat land had not. It is known that potash manures favour the growth of *Leguminosæ*, and in the case of the soils of pasture land, the surface of which is much richer in nitrogen than that of ordinary arable soil, there is evidence that the increased amount of nitrogen taken up, both by the Gramineæ and the Leguminosæ, under the influence of the potash manure is derived from the rich surface soil itself, and probably as nitric acid. Of course, if phosphoric acid and potash in available condition were deficient, their application would of itself enhance the rate of nitrification even in an arable soil poor in nitrogen; but the extremely limited effect of such manures when applied to such soils for the growth of cereals, points to the conclusion that little if any of the excess of nitrogen as nitric acid in the *Trifolium repens* land, compared with that in the wheat-fallow land, is to be attributed to the action of the phosphoric acid and potash independently of the growth of the *Leguminosæ*.

Lastly, in March, 1881, and again in July, 1883, the surface soil of both plots was found to be very low in nitrogen determinable by soda-lime; that of the clover-land containing not much more, and that of the wheat-fallow land rather less, than 0.1 per cent. According to the figures, the leguminous crop soils contained from 400 to 500 lbs. more combined nitrogen per acre in the first 9 inches of depth than the wheat-fallow soil. To the total depth of 108 inches, the plots show an average of not much less than 20,000 lbs. of combined nitrogen per acre; excepting that the *Vicia sativa* plot 6 shows considerably less than the others, owing to the sandy and gravelly character of the samples of its subsoil at the lower depths, whilst the *Trifolium repens* soil, the samples of which were more clayey, shows the highest of the series.

Thus, independently of the application of mineral manures to the leguminous plant plots, the characteristic difference in the history of the two plots now under consideration is—that the one had grown a gramineous crop alternately with fallow for more than 30 years, and

the other had, during the same period, grown six gramineous crops, and frequently been fallow, but it had been sown 12 times with red clover, and during the immediately preceding six years 4 times with white clover. That is to say, the chief distinction is, that the one had, from time to time, especially in the earlier and later years, grown a leguminous crop, whilst the other had not; and the leguminous crop soil is found to contain, down to the depth of 108 inches, nearly three times as much nitrogen as nitric acid as the gramineous crop soil.

The difference is much the greater in the first 18 inches of depth, indicating more active nitrification in the superficial layers; and this is doubtless mainly if not wholly due to the accumulation of more nitrogenous crop-residue from the leguminous than from the gramineous growth. It may here be mentioned that the amount of nitrogen removed in the *Trifolium repens* crops averaged over the preceding four years about 30 lbs. per acre per annum, but the immediately preceding crop (that of 1882) would probably remove between 60 and 70 lbs. How much beyond this would be contained in the crop-residue, and how much it would be in excess of that in the residue from the wheat crop, we have not the means of estimating; but it may safely be concluded that it would be considerably less than sufficient to supply the excess of about 90 lbs. of nitric nitrogen found to the depth examined in the soil of the *Trifolium repens* plot more than in the soil of the wheat-fallow plot; whilst, as has been shown, there was probably a material amount of drainage below that depth, which, according to the figures, would be much richer in nitric acid than any drainage from the wheat-fallow soil.

Part of the increased amount of nitric nitrogen in the lower layers of the leguminous plant soil may, however, also be due to washing down from the surface. On this point, it should be stated that, from September, 1882, to the end of February, 1883, the rain-gauge showed about 24 inches of rain, and the drain-gauges about 18 inches of drainage, so that the autumn and winter conditions had been conducive to both distribution and loss of nitric acid. In March and April there was very little of either rain or drainage; in May there was less than the average amount of rain, but more than the average amount of drainage; in June both rain and drainage were below average. Lastly, in July there was considerably more than average of both rain and drainage, nearly half of each occurring before the commencement of the soil-sampling on the 17th, and most of the remainder before its completion on the 26th.

Thus, not only had the conditions of the previous autumn and winter been favourable for distribution and loss, but the period immediately preceding and during the soil-sampling, which was also that of active

nitrification, were such as to favour distribution, if not even some loss by drainage.

It is, however, not easy to suppose that the whole of the excess of nitric nitrogen in the lower layers of the *Trifolium repens* soil is due to washing down from the surface.

That the increased amount of nitric acid found in the lower layers, not only of the *Trifolium repens*, but also of the *Vicia sativa* soils, is not wholly due to more active nitrification in the surface, and percolation downwards, would appear from the fact that the surface soil of each of the three leguminous plant plots, after more than 30 years of greater removal of nitrogen in produce, due chiefly to the frequent growth of leguminous crops, still remains somewhat richer in nitrogen than that of the wheat-fallow plot. Or, if this is to be attributed to the accumulation of nitrogenous crop residue near the surface, in amount more than compensating for the exhaustion of nitrogen by growth, this means, unless indeed we assume that it has come from the atmosphere, that the nitrogen has been derived from the stores of the subsoil, and if as nitric acid, obviously not wholly from the surface soil.

An obvious difficulty in the way of the assumption that the increased assimilation of nitrogen by the *Leguminosæ* is due to a supply of nitric acid by the nitrification of the nitrogen of the subsoil, is that the direct application of nitrates as manure has comparatively little effect on the growth of such plants. In the case of the direct application of nitrates, however, the nitric acid will percolate chiefly as nitrate of soda or nitrate of lime, unaccompanied by the other necessary mineral constituents in an available form; whereas, in the case of nitric acid being formed by direct action on the subsoil, it is probable that it will be associated with other constituents, liberated, and so rendered available, at the same time.

Upon the whole, the indication certainly is, that nitrification is more active under the influence of leguminous than of gramineous growth and crop-residue.

In Mr. Warington's paper "On Nitrification" (Trans., 1884, 637), he states that samples of subsoil taken at a considerable depth, with precautions to exclude any roots or other organic matter, when introduced into a sterilised nitrogenous liquid, did not induce nitrification; the conclusion being that the subsoil was destitute of nitrifying organisms. This is obviously no proof that the nitrogenous matter of the subsoil would not nitrify if the organisms, with the other necessary conditions, were present. Indeed, results will be adduced further on, pointing to the conclusion that nitrification does take place in subsoils under such conditions.

An obvious conclusion from the results given in the table is that, in

the case of a soil under leguminous growth, the conditions are favourable for the development of the nitrifying organism; but, in what way, the evidence at present at command does not enable us to explain. If, however, this view should be confirmed, an important step would be gained towards the more complete explanation of the source of the nitrogen of the *Leguminosæ*.

In the case of the experiments now under consideration, the large amount of nitrogen as nitric acid was found in the soil where previously the deep-rooting red clover had frequently been sown and failed, but recently the shallow rooting *Trifolium repens* had been grown. The increased amount of nitrogen as nitric acid, not only in the upper but in the lower layers, must therefore have had its source, either wholly in the more active nitrification in the upper layers, and subsequent percolation downwards, against which view reasons have been given above, or it is only in part due to this source, and in a greater or less degree to the passage downwards of the nitrifying organism, and the nitrification of the nitrogen of the subsoil.

On the view here supposed, there would be much less difficulty in accounting for a large amount of the nitrogen of the subsoil thus becoming available to such deep and strong rooted plants as the *Melilotus leucantha*. With the penetration of the roots, channels are formed, by which, in addition to those made by worms, the nitrifying organism may pass downwards in association with recent and decomposable organic matter. There is direct evidence that much water is drawn up, and air, and some water, with its contents, must necessarily go down. We have thus all the conditions necessary for the supply of nitrogen as nitric acid to the roots, provided only the nitrogen of the subsoil is subject to nitrification.

On the assumption, therefore, that leguminous growth and crop-residue are favourable for the development of the nitrifying organism, it would follow that, if the conditions of soil are such as to allow of the establishment of a good plant, and to meet its requirements for mineral food, the greater its root development, the greater will be the amount of nitric acid formed, and of nitrogen so rendered available to the plant from the subsoil.

It is quite in accordance with such an explanation that it is only the deep and strong rooted *Leguminosæ* that yield very large amounts of nitrogen over a given area in their crops. It is further consistent with the supposition that the source of the nitrogen is the soil and not the atmosphere, that when such crops have been grown for some years, and have removed very large amounts of nitrogen, they cannot be grown again on the same land for many years afterwards; the explanation apparently being that, within the range of the roots of the particular plant, the stock of organic nitrogen in a condition

susceptible to nitrification, and perhaps also the supply of the necessary mineral constituents, in an available condition, had been for the time exhausted. It is also consistent with the idea of a soil-source, that when the same description of leguminous plant has been grown year after year until it fails, another description, with different root-habit and root-range, may grow luxuriantly for some years, and then in its turn decline or fail.

There is of course the alternative that the soil and subsoil may be the source of the nitrogen, and yet that the plant may take it up in other forms than as nitric acid, as ammonia, or as organic nitrogen.

We have shown that, in the growth of fungi, as in the case of "*Fairy rings*," both the organic nitrogen and the organic carbon of the soil are much reduced, and there is nothing in the conditions of growth of such plants, so far as they are known, at all inconsistent with the supposition that they take up their nitrogen and carbon directly from organic matter. The evolution of carbonic acid is a characteristic of the accumulative process of such plants; and it is found that the proportion of carbon to nitrogen finally fixed in the plant, is lower than the proportion of carbon to nitrogen lost by the soil.

The characteristic conditions of accumulation and growth of green leaved plants are, however, essentially different; and such as to require that clear experimental evidence should be adduced before the conclusion can be accepted that they take up any material amount of their nitrogen and carbon from the same sources, and in the same manner, as the plants devoid of chlorophyll. Supposing the *Leguminosæ*, for example, were able to take up nitrogen directly as organic nitrogen from the subsoil; it must either be assumed that they take up carbon also, as do the fungi, or that they break up the organic compound, and in some way or other eliminate the carbon—which also must be eliminated in the case of nitrification.

Now, in the ordinary clay subsoil at Rothamsted, the relation of the carbon to the nitrogen is as 6 or 8 to 1, but in our common leguminous crops it is about 15 to 1. Hence, even if the whole of the carbon in association with nitrogen in the subsoil were taken up by the plant, it would not be sufficient to supply the whole of the carbon, and there would still be room for much assimilation from carbonic acid under chlorophyll action.

Or, it may be assumed that only the carbon of the *nitrogenous compounds* of the plant may be taken up with the nitrogen by the roots, from the subsoil. This would require less than $3\frac{1}{2}$ parts of carbon to 1 of nitrogen to be so supplied. So far, however, as direct experimental evidence is available on the point, it is, to say the least, doubtful, whether carbon supplied to the roots even as carbonic acid is

assimilated by green leaved plants; nor are we aware of any experimental evidence showing that such plants assimilate carbon presented to their roots in other forms of combination.

Thus, whilst, so far as existing knowledge goes, physiological considerations seem to militate against the supposition that green leaved plants take up carbon from organic matter in the subsoil, the only ground for assuming that they so take up their nitrogen is that as yet other explanations are quantitatively inadequate to account for the facts of growth.*

In defect of clearer evidence than we at present possess, leading to a conclusion which would approximate rather than differentiate the processes of accumulation of fungi and of green leaved plants, it will be of interest to follow up more closely, clues that seem to promise at least a more consistent solution of our difficulty as to the source of the nitrogen of the *Leguminosæ*.

This brings us to a consideration of the results given in the other columns of the Table II (p. 395).

It has been seen that the *Trifolium repens* soil showed more nitric nitrogen at every depth down to 12 times 9 inches, or in all to 108 inches, than the wheat-fallow soil. But the other columns show that in the case of both plots, where another leguminous plant, the *Vicia sativa*, had yielded fair crops, the amount of nitrogen as nitric acid was very much less. The inference is that the *Vicia* had taken up nitric acid and assimilated its nitrogen.

To go a little more into detail: each of the *Vicia* plots shows less nitric acid, at every depth down to 108 inches, than the *Trifolium repens* plot; but the difference is by far the greatest in the upper layers, and especially in the first 18 inches from the surface; and this is the range within which this plant throws out by far the larger amount of root. But the reduction is very distinct below this point; and the supposition is that water had been brought up from below, and with it nitric acid. In fact, the determinations showed less water in the soils of both the *Vicia* plots, at every depth, excepting the eleventh, than in the corresponding soils of the *Trifolium repens* plot, the eleventh depth of which showed the lowest proportion of soil of any in the whole series of plots and depths, and a very large amount of stones. Reckoning to the total depth of 108 inches, the mean for the two *Vicia* plots shows less water, corresponding to between 6 and 7 inches of rain, or to between 600 and 700 tons of water per acre. Making full allowance for all irregularities at individual depths, or between hole and hole, due to variations in the character of the subsoils, there is here direct proof of much water, doubtless with its soluble contents, having been drawn up from the subsoil.

* The cases of the so-called "Insectivorous Plants" are obviously not parallel.

Calculated per acre, there is, in the one case 81.49 lbs., and in the other 90.98, lbs. less nitrogen as nitric acid in the *Vicia* soils than in the *Trifolium* soil, down to the total depth of 108 inches; nearly half of the deficiency being below the first 18 inches. Even supposing that no more nitrification had taken place in the *Vicia* soils where there was growth, than in the *Trifolium* soil where there was no growth, the difference which the actual results indicate would account for a large proportion of the nitrogen of the crops.

It has been shown, however, that the conditions of the weather had been such as to lead to the conclusion that there was probably some loss of nitric acid by drainage, which would obviously affect the *Trifolium repens* plot, where there was no growth, considerably more than the *Vicia* plots where there was growth, and a constant tendency to the drawing up of water with its contents. It is obvious that, so far as this has been the case, the amount of nitrogen as nitric acid found in the *Trifolium repens* plot down to the depth examined, does not represent the whole that had been formed within those limits. Now the amount of nitrogen as nitric acid remaining in the soil of one *Vicia* plot is estimated at 64.2 lbs. per acre, and the amount of nitrogen in the crop at 126 lbs., in all 190.2 lbs., or about 44.5 lbs. more than was found as nitric acid in the *Trifolium repens* soil; whilst in the case of the other *Vicia* plot, the amount of nitric nitrogen in the soil was estimated at 54.7 lbs., and the amount of nitrogen in the crop at 143.7 lbs., in all, in soil and crop, 198.4 lbs., or 52.7 lbs. more than was found in the *Trifolium repens* plot. On the supposition, therefore, that the whole of the nitrogen of the *Vicia* crops had been taken up as nitric acid, we have to assume that in the one *Vicia* plot 44.5 lbs., and in the other 52.7 lbs., more nitrogen as nitric acid was available than in the *Trifolium repens* plot to the depth examined; and this might be accounted for, partly by less loss by drainage from the *Vicia* plots, and partly by more nitrification under the influence of the growing crops, or their residues.

But, even if it be admitted that the source of the nitrogen of the *Vicia* crops is thus satisfactorily explained for the year in question, it is to be borne in mind that the same plots had grown the same plant in each of the five preceding years, with, on the two plots, an estimated average yield of nitrogen of rather over 40 lbs. in 1878, nearly 47 lbs. in 1879 and in 1880, nearly 70 lbs. in 1881, and between 140 and 150 lbs. in 1882; or an average of about 70 lbs. per acre per annum over the five immediately preceding years. But the amount of nitrogen taken up each year must have been much more than this, as each of the crops must have left nitrogenous crop-residue near the surface, which would yield nitric acid for the succeeding crop or crops. Much of the nitrogen of the removed crops and the residue combined,

must obviously be due to other sources than the original surface soil; and if to the subsoil, it must either have been taken up as organic nitrogen (or ammonia), or, as it would seem in 1883, as nitric acid; and in that case the annual nitrification beyond that of the previous crop-residue near the surface, must have yielded approximately as much nitrogen as was contained in the removed crops. As the *Vicia* crops were large in 1882, so also would their residue be proportionally large, and contribute a correspondingly large amount of nitric acid near the surface for the crop of 1883. But the crop of 1883 was nearly as large, and it, in its turn, would leave a correspondingly large residue, leaving approximately the whole of the nitrogen removed in the crop to be otherwise provided than from previous residue.

In conclusion, in reference to this series of experiments, it must be admitted that, without relying at all rigidly on the exact numerical results obtained under circumstances of so much difficulty as is involved in such an inquiry, these results, taken in conjunction with all that have been before adduced, justify the conclusion that much, if not the whole, of the nitrogen of the *Vicia sativa* crops had been obtained from nitric acid within the soil.

The next Table (III, p. 404), relates to the soil where beans had been grown almost continuously for about 30 years, the land had then been fallow for between 4 and 5 years, to 1882 inclusive, and the stock of nitrogen in the surface soil had been much reduced, and was in fact very low. Barley and clover were sown in 1883. The clover came up extremely well, and was very luxuriant even that year, much interfering with the growth of the barley; and this year, 1884, it has given two heavy crops.

It is certainly contrary to what would be anticipated, that, on this bean-exhausted soil, with its low percentage of nitrogen in the upper layers, very luxuriant crops of clover should be grown. Nor have we any data as to the changes in the soil and subsoil under the influence of this luxuriant growth. It is to be borne in mind, however, that the land had been fallow for several years, that clover had not been grown on it for perhaps 40 years or more, and that it succeeded a crop, though a leguminous one, of very widely different root-habit and root-range. Whether, as the result of the fallowing or not, it is obvious that poor as the surface soil was in total nitrogen, it was in favourable condition, both as to nitrogen and mineral supply, for the establishment of a good plant. This accomplished, it may safely be concluded, that the plant would develop much root in the subsoil, that it would, directly or indirectly, draw up much water from below the surface, and that, with this, it would take up nitrogen as nitric acid, as well as other constituents, from the subsoil.

TABLE III.

Nitrogen as Nitric Acid per acre, lbs., in Soils of Experimental Plots;
Beans many years in succession; Fallow last $4\frac{1}{2}$ years.

Geescroft Field, Rothamsted. Sampled April 9—13th, 1883.

Depths.	Without manure.	Mineral manure		Farmyard manure.
		Alone.	And ammonium salts or nitrate.	
	Plots 1 and 2.	Plot 8.	Plots 9 and 10.	Plot 42.
inches.	lbs.	lbs.	lbs.	lbs.
1—9	4·28	3·34	3·46	13·57
10—18	5·52	6·69	5·81	8·76
19—27	4·81	4·33	4·12	7·70
28—36	2·69	2·33	4·14	8·51
37—45	2·68	1·25	2·28	4·36
46—54	1·90	1·05	2·34	1·85
55—63	2·60	0·81	1·48	1·71
64—72	3·47	0·92	1·75	4·00

Summary.

1—27	14·61	14·36	13·39	30·03
28—54	7·27	4·63	8·76	14·72
55—72	6·07	1·73	3·23	5·71
1—36	17·30	16·69	17·53	38·54
37—72	10·65	4·03	7·85	11·92
1—72	27·95	20·72	25·38	50·46

Not only was the total nitrogen in the surface soil very low (about 0·1 per cent. in the dry sifted soil), but the table affords direct experimental evidence that the amount of nitric acid already existing in the soil when the barley and clover were sown was extremely small. Even in the case of the farmyard manure plot, and much more so in that of the other plots, it was entirely inadequate to meet the requirements of the luxuriant crops of clover.

The soils were sampled from April 9—13, 1883. It has been already stated that the land had been fallow for several years, so that there would be a minimum amount of crop-residue near the surface; and since, during the autumn and winter of 1882—3, there had been a great excess of both rain and drainage, it could not be expected that there would be much of the probably limited amount

of nitric acid formed in the previous summer and autumn remaining in the soil in April. Indeed, excepting in the case of the farmyard manure plot, there is more nitrogen as nitric acid in the second and third, and in one case in the fourth depth, than in the first, thus affording direct evidence of washing down. In fact, in the first three depths, that is, down to 27 inches, there is only about half as much nitrogen as nitric acid as, to the same depth, in the wheat-fallow soil sampled in the following July, and there is also less in the next five depths.

Here, then, we have a surface soil with the total nitrogen very much reduced by previous treatment, and very low, in both surface and subsoil, very small amounts of ready-formed nitric acid, and probably a minimum amount of crop-residue near the surface for decomposition and nitrification, when the red clover was sown. Yet very luxuriant crops were grown, carrying off more than 200 lbs. of nitrogen per acre, and, of course, leaving a highly nitrogenous crop-residue besides.

Whence comes this nitrogen? The alternatives are, 1—that it has been supplied from the atmosphere, in favour of which view there is nothing excepting that it would afford an explanation otherwise not very obvious; 2—that it has been derived directly from the organic nitrogen of the soil and subsoil, for which again there is as yet no proof, whilst there are physiological reasons against it; 3—that under the influence of the once well started leguminous growth, with its excretions and residue, the development of the nitrifying organism is favoured, first in the upper and richer, and afterwards in the lower and poorer layers, and that thus the organic nitrogen of the soil and subsoil has been gradually rendered available for the exigencies of growth; and that the supply was largely derived from the subsoil may be inferred from the fact that, after the growth of clover, the surface soil is generally found to be richer in total nitrogen determinable by the soda-lime method. For this explanation, too, it is freely admitted that proof is wanting; but there is, at any rate, more evidence from analogy in its favour than for either of the other solutions suggested.

The next results relate to plots on which rotation experiments have been conducted through 9 courses of 4 years each, that is, over a period of 36 years in all. The course of cropping has been, 1—roots; 2—barley; 3—clover, or beans, or fallow; 4—wheat. The manures indicated at the head of the columns in the table (p. 406), were only applied for the roots commencing each course, that is, once in 4 years; and the samples of soil were taken after the wheat crop concluding the ninth course, and consequently four years after the last application of manure.

TABLE IV.

Nitrogen as Nitric Acid per acre, lbs., in Soils of Experimental Plots, after Rotation 36 years. Roots; Barley; Clover, or Beans, or Fallow; Wheat.

Agdell Field, Rothamsted. Sampled November 15, 1883, to January 4, 1884.

Depths.	Mineral and nitrogenous manure. Roots fed on the land.		Superphosphate only. Roots carted.	
	Fallow.	Clover or beans	Fallow.	Clover or beans.
	Plots 1 and 2.	Plots 3 and 4.	Plots 13 and 14.	Plots 15 and 16.
inches.	lbs.	lbs.	lbs.	lbs.
1—9	3·44	6·13	3·36	3·66
10—18	3·11	4·41	2·64	3·48
19—27	0·79	1·63	0·95	1·51
28—36	1·01	1·30	0·90	0·96
37—45	0·81	1·52	0·45	1·18
46—54	0·61	0·81	0·53	1·55
55—63	0·77	2·23	1·22	0·85
64—72	0·99	1·68	1·49	1·57
73—81		2·44	2·97	1·67
82—90	2·03	2·08	2·78	2·00
91—99	1·53	2·13	4·81	2·36
100—108	3·75	2·83	3·11	0·90

Summary.

1—27	7·34	12·17	6·95	8·65
28—54	2·43	3·63	1·88	3·69
55—81	2·31	6·35	5·68	4·09
82—108	7·31	7·04	10·70	5·26
1—54	9·77	15·80	8·83	12·34
55—108	9·62	13·39	16·38	9·35
1—18	6·55	10·54	6·00	7·14
19—108	12·84	18·65	19·21	14·55
1—108	19·39	29·19	25·21	21·69

The first two columns of the table show the amounts of nitrogen as nitric acid down to the depth of 12 times 9 inches, or in all to 108 inches, in the soils where a full manure, both mineral and nitrogenous, had been applied every fourth year; and the third and fourth columns show the amounts in those where superphosphate of lime only had been applied, once in four years; the determinations being made, in each case, four years after the application.

Each of these plots is again divided into two—One-half being

left fallow, and the other growing clover or beans, in the third year of the course. That is to say, from one-half—that in fallow—there is no crop, and therefore no nitrogen removed in the third year of the course, whilst from the other a highly nitrogenous leguminous crop, clover or beans, is removed.

A further distinction between the differently manured plots is, that on the highly manured plot the roots were fed on the land, whilst they were entirely removed from the superphosphate plot. Thus, the one plot is not only very much more highly manured, but it is otherwise subjected to much less exhausting treatment.

The soil sampling was conducted between November 15, 1883, and January 4, 1884, the operations being very much interfered with by rain. It has already been stated, that there was a great deal of rain, and a great deal of drainage, during the previous autumn and winter, 1882—3. There was, however, very little drainage in either March or April, a fair amount in May, very little in June, a good deal in July, scarcely any in August; but there were considerable quantities in September, October, November, and December.

Upon the whole, therefore, the conditions during the previous twelve months or more were such as to induce distribution, and loss, of nitric acid by drainage.

The first point to remark is that, under these circumstances, the amounts of nitrogen as nitric acid found are in all cases very small; the highest amount being little more than half as much as was found in the wheat-fallow soil in Hoosfield, sampled before the loss by drainage of August, September, October, and November. Next, there is a general tendency to an increase in the amount in the lower layers, indicating washing down, and probably loss below.

Comparing plot with plot, and taking first the highly manured and less exhausted plot, it is seen that the figures in the two columns are very consistent. The amount of nitrogen as nitric acid is higher at every depth (excepting the twelfth) where clover had been grown, than where the land had been fallow, in 1882. That is to say, where the land had been fallow there was no growing plant to take up the nitric acid formed; there would be a minimum of crop-residue, and the smaller amount of nitric acid would be subject to drainage, both throughout the fallow period, and during the succeeding very wet autumn and winter. On the other portion, the growing clover would take up nitric acid, and leave a highly nitrogenous crop-residue near the surface. There would thus be more nitric acid formed, and remaining, within the range of the soil-sampling; and as a matter of fact the wheat crop of 1883, succeeding the clover, was larger, and took up more nitrogen, than that after the fallow. Indeed, over the 36 years of the experiment, whilst the clover or bean plot has yielded an average of 68·4 lbs.

of nitrogen per acre per annum in the crops, the fallow plot has only yielded 47 lbs.; or deducting the amounts of nitrogen applied in manures, the yield in the crops of the clover or bean plot has been 34 lbs., and that of the fallow plot only 12.6 lbs. per acre per annum.

This experiment affords an illustration of the loss of nitrogen that the land may sustain by fallow in a wet season, and of the benefits arising from the ground being covered with a crop which takes up the nitric acid as it is produced; and obviously the effect will be the greater when that crop is a leguminous one if, as has been suggested, its growth and residue are favourable to the development of the nitrifying organisms, and the formation of nitric acid, the nitrogen of which is conserved by the plant.

We turn now to the results relating to the much more exhausted plot, receiving only superphosphate of lime every 4 years, and no nitrogen in manure, and from which the root-crops are entirely removed instead of being fed on the land. From the fallow portion of this plot, an average of 31.1 lbs., but from the clover or bean portion of 44.4 lbs. of nitrogen has been removed per acre per annum in the crops. In 1882, about 150 lbs. of nitrogen were removed in the crop on the clover portion, the fallow portion losing none except by drainage; and after this the wheat crop of 1883 removed rather more nitrogen from the fallow portion.

The influence of the clover crop residue is nevertheless still seen in the somewhat higher amount of nitrogen as nitric acid in the first six depths; whereas, with the tendency to passage downwards, rather than to drawing upwards, during the fallow period, there is more nitric acid in the lower layers of the fallow portion.

To conclude in relation to the results of these rotation plots:—they do not contribute very direct, or very important evidence, on the main point of our inquiry—that of the soil-source of the nitrogen of our crops generally, and of the *Leguminosæ* in particular; but so far as they go they are found, on detailed examination, to be consistent in their indications with those which have gone before, and which are more definite in character.

The Sources of the Fertility of some Manitoba Prairie Soils.

If then, the mineral constituents not being deficient, and being in available condition, the fertility of a soil is largely to be measured by the amount of nitrogen it contains, and the degree in which it is subject to nitrification, it becomes a matter of interest to determine the characters of virgin prairie soils in these respects.

In our former paper, given two years ago, we gave the determinations of nitrogen in some prairie soils.

In a sample of Illinois prairie soil, supplied some years ago by Sir James Caird to Dr. Voelcker for analysis, the amount of nitrogen found in it by him, and also at Rothamsted, corresponded to 0·25 per cent. in the dry mixed soil and subsoil; while in the separate surface soil Dr. Voelcker found 0·33 per cent.

Again, in 1882 between forty and fifty samples of soil from the North-west Territory, taken at intervals between Winnipeg and the Rocky Mountains, were sent over to the High Commissioner in London for exhibition. They were exhibited in glass tubes 4 feet in length, and were stated to represent the core of soil and subsoil to that depth. Samples of the surface soils of three of these were kindly supplied to us for the determination of nitrogen in them. The following results were obtained :—

	Per cent. nitrogen in dry soil.
No. 1. From Portage la Prairie, about 60 miles from Winnipeg, under cultivation several years.....	0·2471
No. 2. From the Saskatchewan district, 140 miles from Winnipeg, under cultivation less time than No. 1	0·3027
No. 3. About 40 miles from Fort Ellice, a virgin soil.....	0·2500

Now these soils are probably about twice as rich in nitrogen as the average of arable soils in Great Britain, and perhaps about as rich as the average of the surface soils of permanent pasture land; and as their nitrogen has its source in the accumulation from ages of natural vegetation, with little or no removal, except by drainage, and they do in fact yield large crops, it is to be supposed that they are not deficient in the necessary mineral supplies. Indeed, in Dr. Voelcker's report on four Illinois prairie soils, he calls attention to their richness in potash and other mineral constituents; the amount of lime, however, being somewhat low.

In the case of these soils, we did no more than determine the nitrogen by soda-lime. But it is obvious that if the views we have maintained in the preceding part of this paper are correct, it would be a matter of much interest to determine the degree of susceptibility to nitrification of such soils. In a short visit paid by one of us to Manitoba in the autumn of 1882, a few samples of soil were collected for examination, and it was also arranged at Winnipeg that special samples should be collected. But notwithstanding the infallible baggage-cheque system of the American continent, the bag containing the samples was lost, and the special samples from Winnipeg have not yet reached us, but are still promised.

However, the Deputy Minister of Agriculture at Winnipeg, Mr. Acton Burrows, sent a series of samples last year (1883), to be exhibited at the offices of the Canadian Pacific Railway Company in London; and by his directions, and with the kind co-operation of Mr. Begg, the Land Agent of the Company in London, we have been enabled to obtain fair and sufficient samples of those sent over as above referred to. As the Tables V, VI, VII, and VIII, which follow, recording the results, show, one series of samples come from Niverville, one from Brandon, one from Selkirk, and one from Winnipeg. In each case, four samples were taken, representing respectively the first, second, third, and fourth foot of depth.

In all the samples, we have in the first place determined the total nitrogen, and the total carbon.

Samples were then extracted with water, by the aid of the water-pump, and the nitrogen as nitric acid determined in the extracts. The amount of nitric acid so found in the sample as received being very largely dependent on the conditions of moisture and preservation of the sample, the results of the first determinations are of little significance. After the first extraction, each sample, in a suitable condition as to moisture, was exposed in a shallow dish, covered with a glass plate, and all were subject to the same conditions as to temperature, which, however, were not uniform in the different periods. Then, after a given time, at first 28 days, but afterwards generally for a longer and not always a uniform period, the sample was again extracted, and the nitrogen as nitric acid again determined; and as the Tables show, the process was repeated 8 times, the work extending from March, 1883, to April, 1884.

It is obvious that, by repeated extraction, the soluble mineral matters of the soils would be washed out; and it became a question whether the reduced nitrification in some cases might not be due to a deficiency of mineral matter for the development of the nitrifying organisms, or of the formation of nitrates. Hence, after the fourth extraction, potassium phosphate, magnesium sulphate, and calcium carbonate, were added to the samples. It was evident from the character of the extracts that too much of these had been added, and in the fifth extract scarcely any nitric acid was obtained. After this extraction, however, the action recommenced with some energy, and in the Tables the results obtained in the fifth and sixth extractions are given together.

Again, after the seventh extraction, it was decided to see whether the action would be increased if the exhausted soils were seeded with nitrifying organisms. Accordingly, 0.1 gram of rich garden soil was well mixed with each of the subsoils in which the action had much diminished, and the results obtained after this treatment are

given within brackets, thus [], in the last column of each of the Tables.

We now turn to the consideration of the results obtained. The percentages of nitrogen (determined by the soda-lime method) are given in the first column of Table V; and the percentages of carbon, and its proportion to the nitrogen, in the surface soils, are given in Table IX, p. 419. The amount of carbon found, and its proportion to the nitrogen, in some of the subsoils, are, however, so high, that it is obvious the samples were not quite free from particles of undecomposed vegetable residue, although all that was visible was picked out before the samples were submitted to analysis. The subsoil carbon results are therefore not recorded.

The first soil, that from Niverville, about 44 miles west of Winnipeg, had been broken up from prairie five or six years, and had grown 5 crops of cereals.

The percentage of nitrogen in the dry soil of the first 12 inches of depth is 0.261, or nearly twice as high as in the first 6 or 9 inches of ordinary arable land, and about as high as in the surface soil of pasture land, in Great Britain. Even the second 12 inches of depth is richer than our surface arable soils. The third 12 inches is about as rich as the second 9 inches of the Rothamsted soils, but the fourth is low. Here, however, we have a depth of 24 inches very much richer than the first 9 inches of our own arable soils.

The soil from Brandon, about 132 miles west of Winnipeg, was first broken up in 1882, back set in 1883, and grew 25 bushels of wheat per acre that year.

This soil is not so rich in nitrogen as that from Niverville. Still the dry soil of the first 12 inches of depth contains 0.187 per cent. of nitrogen, and is as rich as the first 6 or 9 inches of good old arable soil, and the second 12 inches is about equal to the exhausted surface soil at Rothamsted; the third 12 inches is about equal to the second 9 inches of the Rothamsted soils; but the fourth depth is very poor.

The soil from Selkirk was taken from a farm which had been in cultivation for 25 years, but from a portion near the buildings which had never been broken up.

Here it is seen that there is an extremely high percentage of nitrogen in the first 12 inches of depth (0.618), and in the second 12 inches as high a percentage as in ordinary pasture surface soil (0.264). The third and fourth depths are about as rich as the Rothamsted subsoils. It might be supposed that the first 12 inches had been contaminated by manure from the buildings, were it not that the second 12 inches also shows a high result.

Lastly, the soil from Winnipeg had been broken up from prairie about 5 years, had been ploughed and trenched, had been manured

TABLE V.
Percentage of Nitrogen in some Manitoba Prairie Soils and Subsoils, also Results showing the Amounts of Nitrogen Nitrified, on exposure for given Periods, &c.

Depths.	Per cent. nitrogen in dry soil.	Nitrogen as nitric acid per million dry soil.									
		Periods of exposure.									
		Original.	1st.	2nd.	3rd.	4th.	5th and 6th.*	7th.	8th.†		
<i>Soil from Niverville.</i>											
inches.	per cent.	days.	days.	days.	days.	lost	days.	days.	days.	days.	days.
1-12	0.261	2.70	14.33	9.44	87	45.75	35	lost	79	4.65	49
13-24	0.169	0.18	3.13	3.23	85	1.89	38	4.14	79	0.57	28
25-36	0.069	0.62	0.38	0.35	82	0.34	38	0.11	79	0.24	28
37-48	0.038	0.74	0.44	0.59	74	0.51	38	0.29	79	0.18	28
<i>Soil from Brandon.</i>											
1-12	0.187	0.23	9.13	8.82	87	33.55	35	12.51	79	6.94	49
13-24	0.109	1.50	1.43	1.05	85	3.27	35	5.70	79	2.37	49
25-36	0.072	0.75	4.56	3.81	82	1.05	38	1.71	79	0.24	28
37-48	0.019	1.40	10.52	0.28	74	0.18	38	0.09	79	0.16	28
<i>Soil from Selkirk.</i>											
1-12	0.618	3.94	48.13	34.77	87	58.83	35	24.90	79	21.73	49
13-24	0.264	3.08	113.67	22.74	77	26.61	35	11.30	79	18.61	49
25-36	0.076	0.52	0.99	1.86	71	1.08	35	0.45	79	0.27	28
37-48	0.042	0.31	0.19	0.22	62	0.77	38	0.35	79	0.23	28
<i>Soil from Winnipeg.</i>											
1-12	0.428	132.37	38.09	28.85	88	57.75	35	35.03	79	21.23	49
13-24	0.327	83.19	15.95	24.75	85	24.27	38	17.97	79	3.95	49
25-36	0.168	36.02	12.40	17.64	77	7.94	40	12.02	79	13.63	28
37-48	0.107	11.52	5.70	8.16	57	0.72	45	4.03	79	0.55	28

* In the cases in which the results are given in parentheses, potassium phosphate, magnesium sulphate, and calcium carbonate were added to the soils after the 4th extraction.

† In the cases in which the figures are enclosed within brackets, thus [], the soils were seeded by 0.1 gram of garden soil after the 7th extraction; and the number of days given represents the period after seeding.

‡ Results probably low.

two or three times, and had grown very good crops of potatoes. It is unfortunate that the land had been manured, as an individual sample may, though there is no evidence that in this case it did, contain portions of undecomposed manure. Both the first and the second 12 inches of depth are very rich in nitrogen (0.428 and 0.327)—richer than the average of old pasture surface soils. The third depth is as rich as a good arable surface soil (0.158), and the fourth much richer than the Rothamsted second 9 inches (0.107).

To convey a more definite idea of the relative richness in nitrogen of these Manitoba prairie soils, it may be well to state that the nitrogen in the dry soil of the first 9 inches of depth of the arable soils at Rothamsted is sometimes as low as 0.1 and seldom exceeds 0.14 or 0.15 per cent.; that in the second 9 inches it ranges from 0.07 to little over 0.08 per cent.; in the third 9 inches from under 0.06 to about 0.07 per cent.; and that in the lower depths it is rather lower still. As a further indication of comparative fertility it may be added that old pasture land at Rothamsted contains in the first 9 inches from 0.25 to 0.30 per cent. of nitrogen.

Some soils, however, peaty soils for example, may contain a high percentage of nitrogen, but in such conditions as to be extremely slowly rendered available. What is the condition of the nitrogen of these rich prairie soils in this respect?

This is illustrated in the columns of the Tables showing the amounts of nitrogen as nitric acid found in these soils and subsoils, after exposure for successive periods under suitable conditions as to moisture and temperature. In Table V (p. 412), the quantities are calculated per million dry soil, for each period. In Table VI (p. 415), the amounts per million dry soil, per day, are given. In Table VII (p. 416), the percentage of the original nitrogen, which is nitrified within each period is given. Lastly, in Table VIII (p. 417), an approximate estimate is given of the amounts of nitrogen nitrified per acre, in each soil, at each depth, within each period, and during the total period of the experiments.

In the narrow columns of Table V, the number of days comprised in each period of exposure is recorded; some periods during which the samples were allowed to go and to remain dry, and the action thus arrested, not being included. It was at first intended that the periods should be uniformly 28 days; but owing to the pressure of other work it was impossible to adhere to this, and hence there are irregularities in the results, comparing period with period, in explanation of which the difference in the length of the periods must be taken into account; but they are also in part due to variations of temperature between period and period. On this point it may be stated that the temperature ranged over the several periods as follow:—

	Centigrade.
First period	15—24°
Second period	18—24
Third „	18—31
Fourth „	10—23
Fifth „	3·5—16
Sixth „	4—27
Seventh „	9—26
Eighth „	11—28

It will be seen that in the case of each set of soils the amount of nitrogen nitrified is very much the greater in the richer surface soil than in the poorer subsoils. It is also generally, though not uniformly, greater in the second than in the third, and in the third than in the fourth depth of 12 inches.

The results are, however, arranged in a more comparable form in Table VI, p. 415, which shows the average amount of nitrogen nitrified *per day*, per million of dry soil, over each period. It is there seen that in most cases, especially of the subsoils, the rate of nitrification was much less over the third and fourth than over the first and second periods.

As already said, after the fourth period, mineral constituents were added, but, from the results, obviously in excessive amount, so that over the fifth period there was scarcely any nitrification; and even taking the results of the fifth and sixth periods together, the rate does not appear to have been increased; whilst, over the seventh period compared with the fourth, it is in most cases, and in some of the subsoils, very much reduced. It will be observed that during parts of the fifth and sixth periods the temperature ranged low; but during the seventh period compared with the fourth, there was not much difference.

Lastly, the increase in the rate of nitrification over the eighth period compared with the seventh, in the case of the subsoils which had been seeded by the addition to them of only 0·1 gram of rich garden mould, is very great. These results are enclosed with brackets thus [].

The results as they stand are very striking; and assuming that their indications are not materially vitiated by the fact that some of the subsoils appear from their high amount of carbon to have contained particles of vegetable residue, they are of much interest and significance, affording evidence that the nitrogen of subsoils is subject to nitrification, provided only that the nitrifying organisms, and the other necessary conditions for nitrification, are not wanting.*

* Further experiments on the point are now in progress.

TABLE VI.

Manitoba Prairie Soils and Subsoils. Nitrogen Nitrified *per day per* million dry soil, during successive periods of exposure.

Depths.	Periods of exposure.							Average.
	1st.	2nd.	3rd.	4th.	5th and 6th.	7th.	8th.	

Soil from Niverville.

inches.								
1—12	0·513	0·337	0·526	lost	0 002	0·166	0·190	(0·250)
13—24	0·112	0·115	0·022	0·109	0·040	0·017	[0·238]	0·072
25—36	0·015	0 013	0·004	0·003	0·010	0·009	[0·046]	0·011
37—48	0·016	0·021	0·007	0·008	0·014	0·006	[0·023]	0·012

Soil from Brandon.

1—12	0 326	0·315	0·386	0 357	0·128	0·248	0·170	0·268
13—24	0·051	0·038	0·038	0·163	0·051	0·085	lost	(0·054)
25—36	0·175	0·136	0·013	0·045	0·010	0·009	[0·098]	0 048
37—48	0·019	0·010	0·002	0·002	0 006	0·006	[0·024]	0·008

Soil from Selkirk.

1—12	1·721	1·242	0·676	0·711	0·357	0·776	0·355	0·701
13—24	0·488	0·812	0·346	0·323	0·188	0·486	0·307	0·364
25—36	0·035	0·066	0·015	0·013	0·010	0·010	[0·075]	0·025
37—48	0·007	0·008	0·012	0·009	0·011	0·008	[0·025]	0·011

Soil from Winnipeg.

1—12	1·360	1·030	0·656	1·001	0·290	0·758	0·577	0·693
13—24	0·213	0·884	0·286	0·473	0·276	0·141	0·362	0·348
25—36	0·443	0·630	0·103	0·301	0·138	0·076	[0·487]	0·249
37—48	0·204	0·291	0·013	0·090	0·003	0·020	[0·372]	0·102

The results would thus lend confirmation to the view that, especially in the case of deep-rooted plants, the subsoil may become an important source of nitrogen yielded up to them as nitric acid; for, in addition to the channels formed by worms, such plants will form others by their roots, and by their growth will cause the passage upwards of much water, and so induce the passage downwards, not only of air, but of other matters, nitrifying organisms included.

Table VII, p. 416, shows the *percentage of the original nitrogen*, of

the soils and subsoils, which was nitrified during each, and the total period of the experiments. The last column shows that, over the total period, from 4 to 5 per cent., or more, of the nitrogen of the richer soils and subsoils was so nitrified; but it is obvious that the conditions of these experiments cannot be compared with those of the soils in their natural conditions of exposure, moisture, and temperature.

TABLE VII.

Manitoba Prairie Soils and Subsoils. Percentage of original Nitrogen Nitrified during successive periods of exposure.

Depths.	Periods of exposure.							Total.
	1st.	2nd.	3rd.	4th	5th and 6th.	7th.	8th.	

Soil from Niverville.

inches.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
1—12	0.55	0.36	1.75	lost	0.01	0.18	0.36	(3.21)
13—24	0.11	0.19	0.11	0.24	0.19	0.03	[0.39]	1.26
25—36	0.06	0.05	0.05	0.02	0.11	0.03	[0.19]	0.51
37—48	0.12	0.16	0.13	0.08	0.29	0.05	[0.17]	1.00

Soil from Brandon.

1—12	0.49	0.47	1.79	0.67	0.54	0.37	0.45	4.78
13—24	0.13	0.10	0.30	0.52	0.37	0.22	lost	(1.64)
25—36	0.63	0.53	0.15	0.24	0.11	0.03	[0.38]	2.07
37—48	0.27	0.15	0.09	0.05	0.23	0.08	[0.35]	1.22

Soil from Selkirk.

1—12	0.78	0.56	0.95	0.40	0.45	0.35	0.28	3.77
13—24	0.52	0.86	1.01	0.43	0.57	0.52	0.57	4.48
25—36	0.13	0.25	0.14	0.06	0.10	0.04	[0.28]	1.00
37—48	0.05	0.05	0.18	0.08	0.20	0.05	[0.16]	0.77

Soil from Winnipeg.

1—12	0.89	0.67	1.35	0.82	0.53	0.50	0.66	5.42
13—24	0.18	0.76	0.74	0.55	0.66	0.12	0.54	3.55
25—36	0.78	1.12	0.50	0.76	0.69	0.14	[0.86]	4.85
37—48	0.53	0.76	0.07	0.38	0.02	0.05	[0.97]	2.78

For the same reason, the calculations *per acre*, given in Table VIII. must also be accepted with much reservation. Still the results are

TABLE VIII.

Manitoba Prairie Soils and Subsoils. Estimated Amounts of Total Nitrogen, and of Nitrogen Nitrified, *per acre*, during successive periods of exposure.

Depths.	Total nitrogen per acre.	Nitrogen as nitric acid.							Total.
		Periods of exposure.							
		1st.	2nd.	3rd.	4th.	5th & 6th.	7th.	8th.	

<i>Soil from Niverville.</i>									
inches.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
1—12	7,308	40.1	26.4	128.1	lost	0.04	13.0	26.1	(234.1)
13—24	5,408	10.0	10.3	6.1	13.3	10.1	1.8	[21.3]	72.9
25—36	2,484	1.4	1.3	1.2	0.4	2.8	0.9	[4.6]	12.6
37—48	1,520	1.8	2.4	2.0	1.2	4.4	0.7	[2.5]	15.0

<i>Soil from Brandon.</i>									
1—12	5,236	25.6	24.7	93.9	35.0	28.4	19.4	23.4	250.4
13—24	3,488	4.6	3.4	10.5	18.2	12.9	7.6	lost	(57.2)
25—36	2,592	16.4	13.7	3.8	6.2	2.8	0.9	[9.9]	53.7
37—48	870	2.4	1.3	0.8	0.4	2.0	0.7	[3.1]	10.7

<i>Soil from Selkirk.</i>									
1—12	17,304	134.8	97.4	164.7	69.7	79.0	60.8	48.7	655.1
13—24	8,448	43.7	72.8	85.2	36.2	47.9	43.5	48.2	377.5
25—36	2,736	3.6	6.7	3.9	1.6	2.8	1.0	[7.6]	27.2
37—48	1,487	0.7	0.8	2.7	1.2	2.9	0.8	[2.4]	11.5

<i>Soil from Winnipeg.</i>									
1—12	11,984	106.6	80.8	161.7	98.1	64.3	59.4	79.1	650.0
13—24	10,464	19.0	79.2	77.7	57.5	69.7	12.6	56.8	372.5
25—36	5,688	44.6	63.5	28.6	43.3	39.2	7.7	[49.1]	276.0
37—48	4,045	21.6	30.8	2.7	15.2	1.0	2.1	[39.4]	112.8

not without significance, as conveying an idea of how freely these soils will yield up their nitrogen in an available form, when subjected to favourable conditions of cultivation, and of drainage if need be, favouring aëration, with, at the same time, suitable moisture and temperature. It must be borne in mind, however, that this ready

susceptibility to oxidation of the nitrogen is a source of loss rather than of gain, if the nitrates are not taken up by crops, but are allowed to encourage the growth of weeds, or to be lost by drainage.

It should be added that qualitative examinations lead to the conclusion that these soils are not deficient in the necessary mineral constituents.* They are, in fact, virgin soils of great fertility, accumulated by ages of natural vegetation, with little or no removal. There is abundant evidence that they are capable of yielding large crops; but that, under present conditions, they do not, on the average, yield amounts of produce at all commensurate with their richness compared with the soils of Great Britain which have been under arable cultivation for centuries, there can be no doubt; for, according to official records, their average yield of wheat per acre is even considerably less than that of the United Kingdom.

That the rich prairie soils of the North-west do not yield higher amounts of produce than they do, is due in part to vicissitudes of climate, and to short seasons of growth, but largely to scarcity of labour, and consequent imperfect cultivation, leading, with other disadvantages, to a luxuriant growth of weeds. Then, again, in the early years of settlement, and until mixed agriculture and stock feeding can be had recourse to, and local demand arises, the burning of the straw, and the deficient production, or the disregard and waste, of manure, are more or less unavoidable, but nevertheless very exhausting practices. So long as land is cheap, and labour dear, some sacrifice of fertility is inevitable in the process of bringing these virgin soils under profitable cultivation; and the only remedy is to be found in increase of population. Still, the fact should not be lost sight of, that such practices of early settlement do involve a serious waste of fertility.

It will be of interest here to contrast the condition of soils of very different history, as to their percentages of nitrogen, and so far as we are able, of carbon also.

Table IX, p. 419, shows the characters, in these respects, of exhausted arable soils, of newly laid down pasture, and of old pasture soils, at Rothamsted, of some other old arable soils, of some Illinois and Manitoba prairie soils, and, lastly, of some very rich Russian soils.

From these results there can be no doubt, that a characteristic of a rich virgin soil, or of a permanent pasture surface soil, is a relatively high percentage of nitrogen and of carbon, and a high relation of carbon to nitrogen. On the other hand, a soil that has long been in arable culture is much poorer in these respects; whilst an arable soil under con-

* See reference to Dr. Voelcker's analyses of Illinois prairie-soil, p. 409; also an analysis of a Manitoba prairie-soil, by Dr. J. M. H. Munro, *Chem. News*, April 2, 1885.

TABLE IX.
Nitrogen and Carbon in Various Soils.

	Date of soil sampling.	In dry sifted soil.*			Authority.
		Nitrogen.	Carbon.	Carbon to 1 nitrogen.	
<i>Rothamsted Arable and Grass Soils.</i>					
Roots 1843-52; barley 1853-55; Roots 1856-69; mineral manures	April 1870	Per cent. 0.0934	Per cent. —	Per cent. —	Rothamsted.
Wheat 1843-44, and each year since; mineral manures {	Oct. 1865	0.1119	1.039	9.3	"
	Oct. 1881	0.1012	1.079	10.7	
Barley 1852, and each year since; mineral manures... {	Mar. 1868	0.1202	—	—	"
	Mar. 1882	0.1124	1.154	10.3	
Arable laid down to grass (ten acres), spring 1879.....	Feb. 1872	0.1235	—	—	"
	Feb. 1882	0.1509	—	—	
	(Barnfield), spring 1874	—	—	—	
	(Appletree field), spring 1863	Nov. 1881	0.1740	—	
	(Dr. Gilbert's meadow), spring 1858	Jan. 1879	0.2057	2.412	
	(Highfield), spring (?) 1838	Sept 1878	0.1943	2.403	
Very old grass land (The Park)	Feb. and Mar. 1876	0.2466	3.377	13.7	"

Various Arable Soils in Great Britain.

Mr. Prout's farm, Broadfield, surface	—	0.170	—	—	Voelcker.
" Blackacre "	—	0.107	—	—	"
" Whitemoor "	—	0.171	—	—	"
Wheat soil, Midlothian	—	0.22	—	—	Anderson.
" Eastlothian	—	0.13	—	—	"
" Perthshire	—	0.21	—	—	"
" Berwickshire	—	0.14	—	—	"
Red sandstone soil, England	—	0.18	—	—	Voelcker.

United States and Canadian Prairie Soils.

Illinois, U.S. No. 1.....	—	0.30	—	—	Voelcker.
" " No. 2.....	—	0.26	—	—	"
" " No. 3.....	—	0.33	—	—	"
" " No. 4.....	—	0.34	—	—	"
Portage la Prairie, Manitoba, surface	—	0.247	—	—	Rothamsted.
Saskatchewan district, N.W. territory, surface	—	0.303	—	—	"
40 miles from Fort Ellice, N.W. territory "	—	0.250	—	—	"
Niwerville, Manitoba, 1st 12 inches	—	0.261	3.42	13.1	"
Brandon, " "	—	0.187	2.66	14.2	"
Selkirk, " "	—	0.618	7.58	12.3	"
Winnipeg, " "	—	0.428	5.21	12.2	"

Russian Soils.

No. 1, 12 inches	—	0.607	—	—	C. Schmidt.
No. 2, 8 "	—	0.467	—	—	"
No. 3, 6 "	—	0.188	—	—	"
No. 4, 6 "	—	0.130	—	—	"
No. 5, 11 "	—	0.305	—	—	"
No. 6, 17 "	—	0.281	—	—	"
No. 7, 9 "	—	0.409	—	—	"

* Calculated on soil dried at 100° C.

ditions of known agricultural exhaustion shows very low percentages of nitrogen and carbon, and a low relation of carbon to nitrogen.

In conclusion, it has been maintained by some that a soil is a laboratory and not a mine, but not only the facts adduced in this and in former papers, but the history of agriculture throughout the world, so far as it is known, clearly show that a fertile soil is one which has accumulated within it the residue of ages of previous vegetation, and that it becomes infertile as this residue is exhausted.

Summary and Conclusions.

1. The annual yield of nitrogen per acre in various crops, grown for many years in succession on the same land without nitrogenous manure, was found to be very much greater than the amount of combined nitrogen annually coming down in rain and the minor measurable aqueous deposits.

2. So far as the evidence at command enables us to judge, other supplies of combined nitrogen from the atmosphere, either to the soil or to the plant itself, are quite inadequate to make up the deficiency.

3. The experimental evidence as to whether plants assimilate the free nitrogen of the atmosphere is very conflicting; but the balance is decidedly against the supposition that they so derive any portion of their nitrogen.

4. When crops are grown year after year on the same land, for many years in succession without nitrogenous manure, both the amount of produce per acre, and the amount of nitrogen in it, decline in a very marked degree. This is the case even when a full mineral manure is applied; and it is the case not only with cereals and with root-crops, but also with *Leguminosæ*.

5. Determinations of nitrogen in the soils show that, coincidentally with the decline in the annual yield of nitrogen per acre of these very various descriptions of plant, grown without nitrogenous manure, there is also a decline in the stock of nitrogen in the soil. Thus a soil-source, of at any rate some, of the nitrogen of the crops is indicated. Other evidence pointed in the same direction.

6. Determinations of the nitrogen as nitric acid, in soils of known history as to manuring and cropping, and to a considerable depth, showed that the amount of nitrogen in the soil in that form was much less after the growth of a crop than under corresponding conditions without a crop. This was the case not only with gramineous but with leguminous crops. It was hence concluded that nitrogen had been taken up as nitric acid by the growing crops.

7. In the case of gramineous crop-soils, the evidence pointed to the conclusion that most, if not the whole, of the nitrogen of the crops was taken up as nitric acid from the soil.

8. In the experiments with leguminous crop-soils, it was clear that some at any rate of the nitrogen had been taken up as nitric acid. In some cases, the evidence was in favour of the supposition that the whole of the nitrogen had been so taken up. In others this seemed doubtful.

9. Although in the growth of leguminous crops year after year on the same land without nitrogenous manure, the crop, the yield of nitrogen in it, and the total nitrogen in the surface soil, greatly decline, yet, on the substitution of another plant of the same family, with different root-habit and root-range, large crops, containing large amounts of nitrogen, may be grown. Further, in the case of the occasional growth of a leguminous crop, red clover for example, after a number of cereal and other crops, manured in the ordinary way, not only may there be a very large amount of nitrogen in the crop, presumably derived from the subsoil, but the surface soil becomes determinably richer in nitrogen, due to crop-residue.

10. It was found that, under otherwise parallel conditions, there was very much more nitrogen as nitric acid, in soils and subsoils down to a depth of 108 inches, where leguminous than where gramineous crops had grown. The results pointed to the conclusion that, under the influence of leguminous growth and crop-residue, the conditions were more favourable for the development of the nitrifying organisms, and, especially in the case of deep-rooting plants, of their distribution, thus favouring the nitrification of the nitrogen of the subsoil, which so becomes a source of the nitrogen of such crops.

11. An alternative was that the plants might take up at any rate part of their nitrogen from the soil and subsoil as organic nitrogen. Direct experimental evidence leads to the conclusion that fungi take up both organic nitrogen and organic carbon, but there is at present no direct experimental evidence in favour of the view that green-leaved plants take up either nitrogen or carbon in that form from the soil; whilst there are physiological considerations which seem to militate against such a view.

12. In the case of plots where *Trifolium repens* and *Vicia sativa* had been sown, each for several years in succession, on soil to which no nitrogenous manure had been applied for about 30 years, and the surface soil had become very poor in nitrogen, both the soil and subsoil contained much less nitrogen as nitric acid where good crops of *Vicia sativa* had grown, than where the more shallow-rooted *Trifolium repens* had failed to grow; and the deficiency of nitric nitrogen in the soils and subsoils of the *Vicia sativa* plots, compared with the amount in those of the *Trifolium repens* plot, was, to the depth examined, sufficient to account for a large proportion of the nitrogen of the *Vicia* crops.

13. It may be considered established, that much, if not the whole, of the nitrogen of crops is derived from nitrogen within the soil—accumulated or supplied; and that much, and in some cases the whole, of the nitrogen so derived, is taken up as nitrates.

14. An examination of a number of United States and Canadian prairie soils showed them to be very much richer in both nitrogen and carbon, to a considerable depth, than the surface soil of old arable lands in Great Britain, and about as rich, to a much greater depth, as the surface soil of permanent pasture land.

15. On exposure of portions of some of these rich prairie soils, under suitable conditions of temperature and moisture, for specified periods, it was found that their nitrogen was readily susceptible of nitrification, and so of becoming easily available to vegetation.

16. After several extractions, the subsoils almost ceased to give up nitric acid; but on seeding them with a tenth of a gram of rich garden soil containing nitrifying organisms, there was a marked increase in the rate of nitrification. This result afforded confirmation of the view that the nitrogen of subsoils is subject to nitrification, if under suitable conditions, and that the growth of deep-rooted plants may favour nitrification in the lower layers.

17. Under favourable conditions of season and of cultivation, the rich prairie soils yield large crops; but, under the existing conditions of early settlement, they do not, on the average, yield crops at all commensurate with their richness, when compared with the soils of Great Britain which have been under arable culture for centuries. But so long as the land is cheap, and labour dear, some sacrifice of fertility is unavoidable in the process of bringing these rich virgin soils under profitable cultivation.

18. A comparison of the percentages of nitrogen and carbon in various soils of known history, showed that a characteristic of a rich virgin soil, or of a permanent pasture surface soil, was a relatively high percentage of nitrogen and carbon. On the other hand, soils which have long been under arable culture are much poorer in these respects; whilst arable soils under conditions of known agricultural exhaustion, show a very low percentage of nitrogen and carbon, and a low proportion of carbon to nitrogen.

19. Not only the facts adduced in this and in former papers, but the history of agriculture throughout the world, so far as it is known, clearly show that, pre-eminently so far as the nitrogen is concerned, a fertile soil is one which has accumulated within it the residue of ages of natural vegetation, and that it becomes infertile as this residue is exhausted.

XLV.—*The Chlorination of Phloroglucol.*

By CHARLES S. S. WEBSTER.

I HAVE continued my researches (Trans., 1883, 205) in collaboration with Messrs. Cross and Bevan, on the chlorination of the trihydric phenols, confining my attention chiefly to phloroglucol. It is now some years since Hlasiwetz showed that the action of the halogen, in presence of water, is to resolve this compound into dichloroacetic acid (*Annalen*, 155, 120). He made no attempt to study this decomposition in the successive stages through which it might, with our present knowledge, be presumed to pass, for the reason doubtless that phloroglucol was not then recognised as a phenol. This being now established, the formation of a substituted chlorinated derivative, as a distinct phase of the reaction, preceding the disruption of the benzene-ring, is a well-grounded assumption; and, indeed, the description of the course of the decomposition, given by Hlasiwetz, contains indications of its passing through such a phase. The proof that the reaction actually takes place in this way is the chief result which I have to record, and I shall therefore state at the outset the conditions under which phloroglucol is converted into a trichloro-derivative, $C_6Cl_3(OH)_3$. This compound is obtained by chlorinating the phenol suspended in carbon tetrachloride, in a vessel surrounded by a freezing mixture. Even under these conditions, however, great care must be taken to prevent local heating, as the trichloro-derivative is rapidly resolved, by the action of the chlorine, into acetic derivatives, and that at comparatively low temperatures. For this reason also it is necessary to arrest the reaction before the liquid becomes saturated with the gas. The following are the details of an experiment. About 13 grams of the anhydrous phenol having been finely powdered, and made into a cream with CCl_4 , was introduced into a test-tube of large size, which was plunged into a freezing mixture of ice and salt. A rapid stream of dry chlorine was passed into the fluid mixture, which was stirred from time to time, the passage of the gas being continued for about two hours. At this time, the contents of the tube appeared but little changed, the suspended solid having only a slightly yellower colour than the original phenol. Secondary decomposition had already set in, as was shown by the brisk effervescence of the contents of the tube. The solid was therefore rapidly filtered off, and well washed upon the filter with carbon tetrachloride. I obtained thus 18 grams of the crude product, which still contained some quantity of undecom-

posed phloroglucol. This was easily separated from the chloro-derivative by taking advantage of its much greater solubility in alcohol and water. Finally I obtained the pure trichloro-compound, by crystallisation from its hot aqueous and alcoholic solutions, in the form of slender needles. The identity of the compound, in regard to its empirical composition, was established by the following analytical determinations:—

(a.) Crystallised from water.

0.4130 gram lost 0.0777 exposed 48 hours in a vacuum over H_2SO_4 .

0.3530 „ „ 0.0700 heated at 100° till the weight was constant.

(b.) Crystallised from alcohol of 0.815 sp. gr.

0.3518 gram lost 0.0655 exposed 48 hours in a vacuum over H_2SO_4 .

	(a)		(b)	Calculated
				$\text{C}_6\text{Cl}_3(\text{OH})_3, 3\text{H}_2\text{O}$.
H_2O	18.8	19.7	18.6	19.0

The substance sublimes slowly at 100° , hence the excess of the loss at this temperature. The anhydrous compound melts at 136° (uncorr.); it sublimes freely at a somewhat lower temperature.

0.2232 gram of the anhydrous substance burnt in a stream of oxygen with the usual precautions gave 0.2512 CO_2 and 0.0367 H_2O .

0.1230 gram gave 0.2328 AgCl .

		Calculated.
		$\text{C}_6\text{Cl}_3(\text{OH})_3$
C	30.7	31.3
H	1.8	1.3
Cl.	46.7	46.2

The compound is almost insoluble in water and in benzene in the cold, but is taken up in some quantity on heating. It is more soluble in alcohol, and crystallises in large transparent needles on the slow evaporation of the solvent. It dissolves in hot concentrated hydrochloric acid, crystallising out on cooling in fine needles. It is decomposed on warming with dilute nitric acid with formation of oxalic acid. It is dissolved without change by concentrated sulphuric acid on gentle warming; but on continuing to heat, hydrogen chloride is evolved, and the solution assumes a deep sage-green colour; on pouring this solution into water, a brown resinous substance is precipitated. It is dissolved by alkaline solutions, and is precipitated unchanged on acidifying. The alkaline solution develops a purple colour on standing.

The original solution, filtered from the crude product, was found to contain traces only of chloroacetic acids.

Having thus established that the chlorination of the phenol precedes its resolution under the continued action of the gas, it remained to study the latter under the conditions adopted in the preparation of the trichloro-derivative. The latter was therefore suspended in carbon tetrachloride, and a current of dry chlorine was passed through the liquid, the temperature being maintained at 10° . Rapid decomposition ensued, evidenced by a brisk effervescence and the disappearance of the solid. The solution was found to contain a mixture of chloraldehydes and chloracetic acids, trichloroacetic acid being the chief product.

The action of chlorine on phloroglucol takes place, therefore, in the two stages thus described; the action is limited to the first, *i.e.*, the chlorination of the phenol, at very low temperatures only, and in absence of water: indeed, even when all precautions are observed, it was found impossible altogether to prevent the secondary decomposition. In my earlier attempts, notwithstanding that carbon tetrachloride was used as the distributing medium, and was kept at a low temperature by the employment of a freezing mixture, I repeatedly failed to obtain the derivative above described; on the other hand, I obtained the chloraldehydes and chloracetic acids in large proportion. The only insoluble product formed in such cases was a resinous body from which a crystalline substance was isolated by several recrystallisations from alcohol. It was obtained, but only in minute quantity, in the form of lustrous cubes.* On analysis it was found to contain 47.2 per cent. chlorine. Not only in this respect, but in many of its reactions it resembled the trichloro-compound above described; at the same time its crystalline form and high melting point (above 250°) prove it to be distinct. I am endeavouring to obtain this substance in sufficient quantity to be able to establish its composition.

It might be objected that no evidence has been afforded that the trichloro-compound above described is in reality trichloro-phloroglucol, and the fact that its melting point, 136° , lies so much lower than that of the phenol, 220° , would appear to throw doubt on its identity. On the other hand, the close analogy which it has with the well-known tribromo-derivative, even also in regard to its low melting point—which for the anhydrous tribromophloroglucol I have observed at 148° (uncorr.)—must be regarded in the meantime as establishing for it the simple relationship to the original phenol. At the same time, it is my intention in the course of these researches, by the determination of molecular volumes and in other ways, to obtain such evidence

* The quantity of this resinous precipitate varied from 25 to 30 per cent. of the weight of the phenol taken. It was analysed on two occasions, after precipitation by acid from solution in dilute potash. These preparations contained 48.4 and 46.4 per cent. Cl respectively.

as may be brought to bear on the problems of the constitutional relationships of the derivatives of this group of phenols.

The history of phloroglucol sufficiently proves that it occupies a position which is in many respects anomalous. Hlasiwetz and Habermann (*loc. cit.*) regarded the results of their study of the action of chlorine on this compound as sufficiently demonstrative that phloroglucol is not a phenol, nor, indeed, an aromatic compound at all. The later investigations of Benedikt (*ibid.*, 189) of the exhaustive bromination of phloroglucol, and of Barth and Schreder (*Ber.*, 12, 503), who succeeded in obtaining this compound as the chief product of the fusion of resorcinol with sodium hydroxide, have however established the contrary, and phloroglucol is now regarded as a trihydroxybenzene. This view is confirmed by the results above detailed. Still its relationships are in many respects anomalous, and afford at least suggestions of a closer connection between the great groups of the aromatic compounds and the carbohydrates than has yet been brought to light. It is from this point of view that this work was undertaken and is being prosecuted.

I wish to express my sense of obligation to Professor Ramsay and the authorities of University College, Bristol, and to Mr. R. E. H. Goffin and the authorities of the United Westminster Schools for the privilege of occupying the laboratories of these institutions for the purposes of this research.

XLVI.—On the Unit adopted for the Atomic Weights.

By LOTHAR MEYER and KARL SEUBERT.

THE dispute which arose immediately after Dalton first enunciated his atomic theory as to unit to which the atomic weights should be referred has for more than half a century divided the chemical world into two camps. Whilst Dalton, and more recently Leopold Gmelin, adopted the smallest atomic weight, that of hydrogen, as their unit, on theoretical and philosophical grounds, Wollaston and Berzelius preferred that of oxygen, partly because they laid less stress on theoretical considerations, but more especially from the purely practical point of view that most of the elements may be compared with oxygen directly, and with hydrogen only indirectly. After Dalton's unit—that of hydrogen—had universally gained the upper hand, for years the old dispute appeared to be settled, and it was to be hoped

that the more accurate investigation of the laws which govern the numerical coefficients of the atomic weights, begun in later times, might be carried out from one point of view. Unfortunately, however, it would appear that this reasonable hope is not to be fulfilled, for once more the old Wollaston-Berzelius theory has cropped up, although in an altered, but, as we consider, a more dangerous form.

As is well known, J. S. Stas,* from his own observations and from those of others, has deduced the highly probable conclusion that the atomic weight of oxygen is not quite 16 times as great as that of hydrogen, but rather about $\frac{1}{100}$ of its value less than 16 H. This follows from—

1st. The numerous gravimetric results obtained by gas analysis since Gay-Lussac and Von Humboldt's discovery, or, what amounts to the same thing, from Avogadro's law, and the experimental estimation of the vapour-densities of oxygen and hydrogen (see our calculation of atomic weights,† No. 1a, and Julius Thomsen's, *Ber.*, 3, 927).

2nd. The synthesis of water by means of copper oxide (*loc. cit.*, No. 1c, d).

3rd. The relation of ammonium chloride to silver nitrate, and of both to silver (*loc. cit.*, Nos. 47 and 83), where the atomic weight of nitrogen ($N = 0.87791$. O) used in the calculation can be confirmed by the relation of both the chlorine and the metal to the nitrate (Nos. 131, 132, 133, 135).

Further, if perhaps with less certainty, from—

4th. The relations of the crystallised and anhydrous strontium chlorides to one another and to silver (Nos. 65, c, and 140).

5th. The relations of anhydrous and crystallised strontium chlorides to one another and to the sulphate (No. 197).

6th. The corresponding numbers for crystallised and anhydrous barium chlorides and silver (Nos. 66e and 141).

7th. The relations of both forms of barium chloride to the sulphate (No. 188d).

8th. From the relation of metallic aluminium to hydrogen and to water (Nos. 8c, d, and 144).

Estimations made according to sections 1 and 2, and yielding results whose accuracy is unquestioned, give a mean which coincides with the proportion $H : O = 0.06265 : 1 = 1 : 15.96$. This Stas also considers to be the nearest to the truth, whilst the rational proportion required by Prout's law $H : O = 0.0650 : 1 = 1 : 16.00$, which has been confuted by numerous observations, is sometimes quite outside the

* *Nouvelles Recherches sur les lois des Proportions Chimiques*. Bruxelles, 1865, p. 24, and elsewhere.

† *Die Atomgewichte der Elemente aus den Originalzahlen neu berechnet*. Leipzig, 1883.

experimental determinations, sometimes close to the limit. To an unprejudiced mind, therefore, having no bias in favour of either hypothesis, there can be no ground for preferring this simple relation to the number deduced from the mean of the observations. Moreover, if the whole number be accepted, the results obtained under sections 3 to 8 in almost all cases give results far less concordant than if the mean be taken, and in the determinations under section 3, the difference between the theoretical and observed numbers is actually greater than the experimental error.

As, however, the relation of the atomic weight of hydrogen to oxygen had not been so accurately ascertained as that of several other elements to one another, Stas, in order to show that Prout's hypothesis was quite untenable, reckoned out all his atomic weights according to what he considered to be the incorrect supposition, that the atomic weight of oxygen is precisely 16 times that of hydrogen. He pointed out that even on this supposition, beyond all measure favourable to Prout's hypothesis, it did not hold good for the other atomic weights. The adoption of Prout's figures by Stas in this case, which was merely hypothetical and done in order to ascertain whether conditions so favourable to Prout's view would confirm them or not, seems now often to be misunderstood, as indicating that the values $O = 16.00$ or $O = 15.96$ might be employed indifferently, which is not the case. Rather it is in the highest degree probable, if not certain, that whilst there is an error of from 0.03 to 0.05 in the coefficient $O = 16.00$, with the mean 15.96 the error is 0.01, or at most only 0.02.

As up to this time chemists had been accustomed to consider $O = 16.00$, and as Stas naturally only discussed the atomic weights recently determined by him, a choice had to be made between the laborious recalculation of all the atomic weights on the basis of the new values for O, Ag, Cl, &c., or to use the old numbers provisionally and to insert Stas' corrected atomic weights in the somewhat incongruous system. The latter easy but incorrect way was adopted by many chemists. This took place the more readily as most of the atomic weights used were rightly regarded as being more or less uncertain, so that a difference of $\frac{1}{100}$ of the weight of oxygen seemed of very little practical importance.

The reasonable hope that the recalculation of all the atomic weights would at least put an end to the old contention as to the most advisable unit weight to be adopted, has unfortunately not been fulfilled. Although it has been universally agreed to abandon the unit $\bar{U} = 1 = 10$ or $= 100$ as used by Thomson, Wollaston, and Berzelius, and to adopt hydrogen as the unit, there is much difference of opinion as to how this is to be done. As with some few excep-

ions (e.g., B, Al, No. 8c, d) the relation of the atomic weights to that of hydrogen can only be determined indirectly through oxygen; the accuracy of all the atomic weights must depend on that of oxygen. Acting on this consideration, we have in our recalculation of the atomic weights, referred to above, retained the unit $O = 1.00$ employed by Wollaston and Berzelius, along with the customary $H = 1.00$. So that in case of a new authentic estimation of the relation $H : O$, the numbers referred to hydrogen as unity can easily be corrected. Some little time ago G. F. Becker* calculated out all the atomic weights, on the supposition that $O = 16.00$, whilst F. W. Clarke†, has, as is the case in our calculations, considered hydrogen equal to unity; but, from a prejudice in favour of Prout's theory, he has constructed a table in which $O = 16$, whilst $H = 1.0023$. T. Sebelien‡ adopts the units employed by us ($H = 1$ and $O = 100$), although he also occasionally inserts numbers reckoned on the supposition that $O = 16$. W. Ostwald§ does not recognise the conclusion arrived at by Stas, that the coefficient $O = 16$ is too high, but makes use of the last five observations of Erdmann and Marchand,|| and rejects the three first, from which it follows that if $H = 1$ then $O = 16$ exactly, whilst the sum of all the researches of the authors named gives $O = 15.96$. J. D. van der Plaats¶ also is inclined to consider that $O = 16$, although he leaves the question open. W. Dittmar** has recalculated the atomic weights published by us (in which $H = 1$) on the supposition that $O = 16$ and $H = 1.0024$.

As a consequence of these different views, all the other atomic weights will differ by 0.25 per cent. of their value, amounting to as much as half a unit with the highest. Everyone will agree that this is undesirable, and also that the smallness of the difference increases the liability to mistakes and confusion, especially when authors give no indication as to what unit they adopt. It is more difficult to say how this inconvenience is to be avoided. In the first place, it must be allowed that both the proposed values of oxygen lie within the limits of experimental error; moreover, if some constant source of error should tend to lower the results, it would be permissible to adopt the maximum value 16.03 instead of the mean value $O = 15.96$. It is more dubious, however, to take the round number, 16.00, for which

* "Atomic Weight Determinations: a Digest of the Investigations published since 1814." Washington Smithsonian Institution, 1880.

† "A Recalculation of the Atomic Weights." Washington Smithsonian Institution, 1882.

‡ *Beiträge zur Geschichte der Atomgewichte. Preisschrift*: Braunschweig, 1884.

§ *Lehrbuch der allgemeinen Chemie*, Leipzig, 1884.

|| Our calculation No. 1d; see also Clarke, *loc. cit.*, p. 5.

¶ *Compt. rend.*, Jan. 5, 1885, 100.

** Tables to facilitate chemical calculations. 2nd edition. Glasgow, 1885.

there is no evidence, except Prout's refuted hypothesis. The secret or avowed preference for this hypothesis seems to be the true motive for adopting this number. We, however, willingly allow that there may be some grain of truth hidden in Prout's theory, but this does not alter the fact that this hypothesis, as at present set forth, is quite untenable. Up to the present time wherever determinations have been made with sufficient accuracy, it has always turned out that the atomic weights are not exactly whole numbers, and this result does not depend on the relation of hydrogen to oxygen. Say what one will, irrational or fractional numbers have been found for the most accurately determined atomic weights. That which is most worthy of note in Prout's hypothesis is best considered, and, indeed, less disadvantageously, when that relation of O to H is adopted which is in accordance with the most authentic observations. Thus it is worthy of remark, that the atomic weights of nearly a quarter of the elements are almost exact

Multiples of Half the Atomic Weight of Oxygen (O=15.96, H₂O=7.98).

Factor.	Product.	Observed atomic weights.	Differences.
1	7.98	—	—
2	15.96	O = 15.96	—
3	23.94	Mg = 23.94	—
4	31.92	S = 31.98	+ 0.06
5	39.90	Ca = 39.91	+ 0.01
6	47.88	Ti = 48.01	+ 0.13
7	55.86	Fe = 55.88	+ 0.02
8	63.84	—	—
9	71.82	Ekaalicon	—
10	79.80	Br = 79.76	- 0.04
11	87.78	—	—
12	95.76	Mo = 95.90	+ 0.14
13	103.74	Ru = 103.50	- 0.24
14	111.72	Cd = 111.70	0.00
15	119.70	Sb = 119.60	- 0.10
16	127.68	—	—
17	135.66	—	—
18	143.64	Di = ?	—
19	151.62	—	—
20	159.60	—	—
21	167.58	Eb = ?	—
22	175.56	—	—
23	183.54	W = 183.6	+ 0.06
24	191.52	Os = ?	—
25	199.50	Hg = 199.80	+ 0.30
26	207.48	Bi = 207.3	+ 0.18
27	215.46	—	—
28	223.44	—	—
29	231.42	Th = 231.96	+ 0.54
30	239.40	U = 239.80	+ 0.40

multiples of half the atomic weight of oxygen or the equivalent weight as determined by the above-mentioned relation.

Such coincidences are worthy of note, but to rectify other atomic weights by them is as unjustifiable as to make the atomic weights round numbers.

For any one, however, who neither supports Prout's hypothesis nor holds the opinion that the observations coincide best with the relation $O : H = 16 : 1$, there seems to us to be not the smallest justification for preferring the value $O = 16$ to $O = 15.96$. For if 16 be taken as the atomic weight of oxygen rather than 1, or 10, or 100, it can merely be for the reason that it seems to be more convenient to take hydrogen as the unit. This in fact seems generally to be intended, but as it is thought that this relation to oxygen is not certain by some thousandths, it is considered better to use the round number 16 provisionally in place of that experimentally determined, viz., 15.96, although it then becomes necessary to make $H = 1.0025$, that is to take $\frac{1}{1000}$ of the atomic weight of hydrogen as the unit. Such an irregular unit can only be allowable in the secret hope in the future fulfilment of Prout's law. No one would surely permanently burden science with such an anomaly.

Further it must be allowed that the atomic weights of all the other elements will vary in the fourth and following figures with that of oxygen, whilst their relative value in many cases has been definitely fixed to the fourth, and even in some cases the fifth place. No hypothetical considerations can alter this fact. Even if to-morrow the relation $O : H$ should be determined with certainty to within one or two thousandths of its value, and be found to differ from the number now accepted, all the other atomic weights would have to be recalculated.

We cannot see what advantage could be derived from provisionally calculating on the hypothesis that $H = 1.0025$ and $O = 16$. That the coefficients of oxygen, carbon, and a few others have been shortened to two figures can hardly be of such advantage as to justify the use of a unit which is not far from being absurd.

It has been asserted, however, that the errors introduced into calculations by considering $H = 1$ are less than the unavoidable experimental errors themselves, but even when this is the case it may well be asked why should even a small error be introduced when it can be avoided? Even without this are not our determinations already sufficiently burdened with sources of error of all kinds? It is, however, not universally the case that a disregard of these small fractional parts in the decimal place, which are ordinarily not taken into account in analyses, have no influence. Even when it causes no difference in most inorganic analyses, it is quite otherwise in the analysis of

organic bodies. No one, of course, would desire to make the calculation using $H = 1.0025$; but considering $H = 1$, and using either

$$O = 15.96 \text{ and } C = 11.97$$

$$\text{or } O = 16.00 \text{ and } C = 12.00$$

differences are obtained in the calculation which under certain circumstances are actually greater than the differences in the composition of closely allied organic compounds. The following table gives the percentage of hydrogen and carbon for the paraffins containing 30 and 31 carbon atoms, and also of the alcohols and the acids derived from them (myricyl alcohol and melissic acid), and also the corresponding amounts of water and carbonic anhydride are given in percentages on the weights of the compounds analysed. The results in the columns headed *a* are reckoned for $O = 15.96$ and $C = 11.97$; those under *b*, $O = 16.00$ and $C = 12.00$.

	H ₂ O.		H.		CO ₂ .		C.	
	<i>a.</i>	<i>b.</i>	<i>a.</i>	<i>b.</i>	<i>a.</i>	<i>b.</i>	<i>a.</i>	<i>b.</i>
C ₃₀ H ₆₂	132 22	132 23	14 723	14 692	312 68	312 80	85 277	85 308
C ₃₁ H ₆₄	132 10	132 11	14 710	14 679	312 73	312 84	85 290	85 321
C ₃₀ H ₆₂ O	127 39	127 40	14 186	14 155	301 26	301 37	82 163	82 192
C ₃₁ H ₆₄ O	127 42	127 43	14 190	14 159	301 66	301 77	82 272	82 301
C ₃₀ H ₆₀ O ₂	119 46	119 47	13 303	13 274	291 94	292 04	79 620	79 646
C ₃₁ H ₆₂ O ₂	119 74	119 74	13 334	13 305	292 61	292 70	79 802	79 828

As is seen, the amount of water according to either calculation is almost identical, as the errors compensate one another; the hydrogen, however, varies by some hundredths, as does also the carbon, whilst the difference in the carbonic anhydride falls in the first place of decimals, and in the case of the hydrocarbons is actually greater than the difference between the hydrocarbons, differing by CH₂. This becomes even more noticeable if the percentages of carbon and carbonic anhydride calculated in both ways in a series of hydrocarbons are compared, as in the accompanying table.

	C ₂₄ H ₅₀	C ₂₆ H ₅₂	C ₂₈ H ₅₄	C ₂₇ H ₅₈	C ₂₈ H ₅₈	C ₂₉ H ₆₀	C ₃₀ H ₆₂
85 176	85 196	85 214	85 232	85 248	85 263	85 277	
207	85 227	85 246	85 263	85 279	85 294	85 308	
312 310	312 384	312 452	312 516	312 575	312 630	312 681	
12 426	312 505	312 588	312 632	312 690	312 745	312 796	

It will be seen that calculations made under *a* or under *b* would lead to quite different interpretations of the analysis. If, for example, it be found by combustion that a hydrocarbon gave 312·5 mgrms. of CO₂ for every 100 mgrms. of substance, the advocate of Prout's law would consider that the results of the analysis would best be expressed by the formula C₂₆H₅₂, whilst according to Stas and his followers the analysis agrees with the formula C₂₇H₅₆. Now no one would of course think of determining the formula of such a body by the analysis alone, but in the choice of the formula it is customary to attach weight to the mean obtained from a series of concordant analyses, and this would lead to error if a mistake of a few thousandths in the atomic weight of hydrogen is considered as of no consequence.

Therefore, whoever agrees with us in considering that the proportion H : O = 15·96 : 1 = 1 : 0·06265, as being the result of the most accurate experimental determinations hitherto made, is more probably correct than O : H = 16·00 : 1 = 0·06250 as required by Prout's law, is guilty of gross inconsistency if he uses the atomic weights O = 16·00, C = 12·00, Cl = 35·46 or 35·5, &c. Of course these figures may be used in the laboratory for approximate calculations, or in preparation work, but they should be altogether discountenanced in calculations of the results of accurate analyses. We would ask the advocates of Prout's hypothesis to lay to heart the question as to whether the general acceptance of a universal basis for all the atomic weight determinations is not of more value than suppositions which in some few cases may possibly not be without foundation.

Every one allows that the relation advocated in this paper (and also all the other atomic weights referred to H = 1) is not yet established to within some few thousandths of its value. Let us then adopt without any reservation the mean value obtained by the concordant results of investigations which have been made in entirely different ways, and await in the future the further examination and establishment of these results by experimental methods. When this has been done we shall be ready amongst the first to make the necessary changes in the calculated values of the atomic weights.

XLVII.—*The Atomic Weight of Silver and Prout's Hypothesis.*

By LOTHAR MEYER and KARL SEUBERT.

As is well known, the calculation of numerous atomic weights is based on that of silver, so that the most accurate determination of the latter is necessary for ascertaining the atomic weights of the elements with certainty; and without this a criticism of Prout's hypothesis as far as regards its foundation in fact does not seem possible.

On this account Stas, in his classical researches, took the greatest pains to ascertain the exact gravimetric relation of silver to oxygen, and to establish it with the most marvellous accuracy by indirect methods.

Stas' researches do *not* by any means confirm Prout's theory that all atomic weights may be expressed by whole numbers, multiples of that of hydrogen, and even if the relation of oxygen to hydrogen = 15.96 : 1 be rejected as doubtful and Prout's relation 16.0 : 1 be used instead, the atomic weights of silver and a number of other elements, amongst which are some of the most accurately determined coefficients, differ far more from whole numbers than can be accounted for by experimental errors. The accuracy and trustworthiness of Stas' results appear, however, to be above all question, so much so indeed that one of the most famous supporters of Prout's theory could only reconcile the contradiction between practice and theory by calling in question the possibility of obtaining chemically pure substances, or indeed it would seem even by doubting the constancy of chemical proportion, the foundation of the atomic theory.*

In the year 1878 Dumas, who was also a most jealous defender of Prout's hypothesis, published the result of some researches in which he had been able to obtain oxygen from pure silver, which had been fused with borax and potassium nitrate. One kilo of the silver was heated to redness in a Sprengel vacuum, and the oxygen given off was collected and measured. In this way 82, 226, 140 and 249 mgrms. of oxygen were obtained from 1 kilo of silver.

Now as Stas in his researches had employed silver which had been melted with borax and nitre, it might, as Dumas points out (*Compt. rend.*, 86, 65—71; *Ann. Chim. Phys.*, [5], 14, 289) also have con-

* Marignac, *Archives des Sciences Physiques et Naturelles* (Nouv. Pér), t. ix, 1860, p. 105. *et seq.* "Il ne m'est pas absolument démontré, que bien des corps composés ne renferment pas constamment et normalement un excès, très faible sans doute, mais sensible dans des expériences très-déliées de l'un de leurs éléments." Compare Marignac (*Ann. Chem.*, Suppl. iv, p. 202).

tained oxygen. In spite therefore of all the care and skill of the experimenter, his researches with metallic silver are thought to be vitiated by a constant error which tends to make the atomic weight of silver too great and that of the halogen too small. The relation of silver to chlorine, instead of being 108 : 35·47, as hitherto accepted, should be 108 : 35·5, which is in accordance with Prout's law.*

It cannot be denied that Dumas' objection is most important; and if Stas really worked with silver containing oxygen the error introduced into his researches would consist in his having employed 999·751 parts of silver instead of 1000 parts.†

By converting silver into the chloride by four different methods Stas obtained: ‡

From 969·3548 grams Ag, 1287·7420 grams AgCl.

From which $\text{Ag} : \text{AgCl} = 1 : 1·32845$.

On applying Dumas' correction, this relation becomes altered into 969·1134 grams Ag = 1287·7420 grams AgCl, that is, $\text{Ag} : \text{AgCl} = 1 : 1·32872$.

Similarly for the conversion of silver by simple synthesis into the bromide and iodide. In all these cases, the possible error may reach the maximum observed by Dumas. Fortunately, however, there are a number of researches made by Stas in which the highest limit of the oxygen present in the silver can be estimated. These are the complete syntheses of silver bromide and iodide, in which not only the compound obtained but both elements were separately weighed.

In both cases the weight of the product was found to be slightly too low, which may be ascribed to oxygen present in the silver.§ Thus the complete synthesis of silver bromide gave (*loc. cit.*, p. 57, No. 42b, β) :

$$\text{Ag} : \text{Br} : \text{AgBr} = 210·5711 : 156·0098 : 366·5639 [4].$$

$$\text{Ag} + \text{Br} \dots\dots\dots = 366\,5809$$

$$\text{AgBr obtained} \dots\dots = \underline{366·5639}$$

$$\text{Difference} \dots\dots\dots = 0·0170$$

This reckoned on the silver employed gives in the most unfavourable

* A conclusion of Dumas, which is questionable in more than one particular. See below.

† That is accepting the most unfavourable case which Dumas has adduced, in which the silver contains 0·249 part of oxygen per thousand.

‡ Lothar Meyer and Karl Seubert, *Die Atomgewichte der Elemente*, 1883, pp. 55 and 56, No. 41g. For the sake of brevity we refer to this work.

§ As the difference in the synthesis of silver bromide was less the more carefully the bromine was dried, it must at least to a certain extent be due to the presence of moisture in the bromine. Washing the precipitate may also have been the cause of slight loss.

case 0.08073 parts of oxygen per 1000, and the corrected weight of silver will be 210.5541 grams.

$$\begin{aligned}\text{Ag : AgBr} &= 210.5541 : 366.5639 \\ &= 1 : 1.74095 \\ \text{in place of} & \quad 1 : 1.74081.\end{aligned}$$

Similarly in the complete synthesis of silver iodide the weight of the product was less than the sum of the weights of the silver and iodine taken: Stas found (*loc. cit.*, p. 59, No. 43*bg*).

$$\begin{aligned}\text{Ag : I : AgI} &= 324.2571 : 381.1262 : 705.3718 [5] \\ \text{Ag + I} &= 705.3833 \\ \text{AgI obtained} &= 705.3718 \\ \hline \text{Difference} &= 0.0115.\end{aligned}$$

This difference corresponds with 0.03547 part oxygen in 1000, and the actual amount of pure silver employed reckoned on this, is 324.2456 grams: consequently—

$$\begin{aligned}\text{Ag : AgI} &= 324.2456 : 705.3718 \\ &= 1 : 2.17542 \\ \text{instead of} & \quad = 1 : 2.17535.\end{aligned}$$

The comparison of the above results with those obtained by the analysis of the chlorate, bromate, and iodate gives the relation of silver to oxygen. Stas found—

$$\begin{aligned}\text{AgClO}_3 : \text{AgCl} &= 398.3177 : 298.4250 [2] \text{ (} \textit{loc. cit.}, \text{ p. 47, No. 35} \textit{b}), \\ \text{AgBrO}_3 : \text{AgBr} &= 188.5332 : 150.1671 [2] \text{ (} \textit{loc. cit.}, \text{ p. 47, No. 36),} \\ \text{AgIO}_3 : \text{AgI} &= 331.6101 : 275.3235 [3] \text{ (} \textit{loc. cit.}, \text{ p. 48, No. 37} \textit{b}), \\ \text{that is, AgCl : O} &= 8.9614 : 1, \\ \text{AgBr : O} &= 11.742 : 1, \\ \text{AgI : O} &= 14.6742 : 1.\end{aligned}$$

It is obvious that not one of these results is affected by Dumas' correction, as the silver is not weighed in the metallic state.

From these the relationship of silver to oxygen is calculated by the formula (*loc. cit.*, p. 50—52)—

$$\frac{\text{Ag}}{\text{AgR}} \cdot \frac{\text{AgR}}{\text{O}} = \frac{\text{Ag}}{\text{O}},$$

in which R represents one of the halogens Cl, Br, or I.

$$\begin{aligned}\text{Ag : O} &= \frac{8.9614}{1.32872} = 6.7439 : 1. \\ \text{Ag : O} &= \frac{11.742}{1.74095} = 6.7446 : 1. \\ \text{Ag : O} &= \frac{14.6742}{2.17542} = 6.7455 : 1.\end{aligned}$$

Of these numbers, none of which agrees with the coefficient 6.7500 required by Prout's law, the third is, however, undoubtedly the most trustworthy, for the first is influenced by the application of a perfectly arbitrary correction, in the second the correction introduced for the presence of oxygen is certainly partly due to another impurity, but the third is obtained by experiments with what are absolutely the very purest materials. This number 6.7455 for the relation between silver and oxygen obtained by applying Dumas' correction to the complete synthesis of silver iodide and by the analysis of silver iodate, is also the mean of the whole of Stas' other determinations, which fluctuate between 6.7451 and 6.7458; it is moreover almost identical with the number 6.7456, obtained from silver iodide and iodate without the application of Dumas' correction, as also with 6.7456, obtained by the reduction of silver sulphide and sulphate.

The conclusion is therefore justified that as Stas' collective researches agree satisfactorily amongst themselves, and also with the results obtained in such a manner as necessarily to be quite free from the error which Dumas has pointed out, the effect of the latter lies within the limits of error and may therefore be neglected. It seems to be quite inadmissible to introduce the maximum of these sources of error, and on the values obtained in this way to endeavour to found an experimental basis for the theory.

Although it seems strange that the silver employed by Stas for the estimation of the atomic weights exhibited only such a slight impurity, whilst the amount of oxygen found by Dumas was very considerable, it must be borne in mind that it is only the oxygen contained in the silver in the *condensed state* that affects the weight, that in the gaseous form and under normal pressure has no more influence on the weight of the silver than the surrounding air. Stas also invariably heated the silver to a dull red heat immediately before weighing it, whereby the greater part of the "occluded" oxygen was doubtless given off or rendered gaseous.

The foregoing observation shows also what we have previously advanced, that Stas' estimations of the atomic weight of silver are not directly influenced by the presence of oxygen in the silver.

The atomic weight of silver is consequently—

(H = 1 and O = 15.96) Ag = 107.66, and (O = 16) Ag = 107.93,

whilst with Dumas' correction applied to the numbers obtained from the experiments with metallic silver and silver chloride—

Ag = 107.63, when O = 15.96,
and = 107.90, when O = 16.

It is evident that the application of Dumas' correction removes the atomic weight of silver further from the whole number required by Prout's hypothesis. Chlorine also = 35.478 ($O = 16$) still remains unreconciled with the theory, whilst some other elements as K, Na, &c., approach nearer to or are removed further from whole numbers, accordingly as O is regarded as equal to 16 or 15.96.*

Dumas, in order to obviate such exceptions to Prout's law as for instance chlorine exhibits, has assumed that hydrogen itself consists of ultimate atoms, of which he at first considered two to be combined to form one atom of hydrogen; but as theory also was found not to agree with the experimental results, he regarded the hydrogen atom as consisting of four of these primitive atoms. In this way, however, the ground of Prout's hypothesis was given up, and hydrogen displaced from its position as the fundamental atom. But even this elastic modification, as Clarke has aptly called it, can only be reconciled with Stas' experimental results by constantly varying the unit, that is, the weight of the ultimate atom, as the accuracy of the experimental determinations increases.

In recent times† some have gone so far as to select the æther, to which they ascribe an atomic weight of 0.0001 (hydrogen being considered as unity), as the fundamental matter from which all other elements are built up. If this number be accepted, it is quite evident that all other atomic weights will necessarily be multiples of it, as none of them have been determined accurately to the fourth, and many others only to the first place in decimals.

It cannot be wondered at, as is shown elsewhere‡, that each atomic weight can be approximately expressed by the formula

$$y = p15 - 15(0.9375)^x,$$

$$\text{or } y = 15(p - [\frac{1}{16}]^x).$$

in which p varies from 1 to 16, and the value of x from 1 to 50, or even to infinity; the fraction $\frac{1}{16}$ approximates so closely to a whole number that any number may be accurately expressed in decimals by the above formula.

Such ingenious speculations are incapable of experimental demonstration, and cannot therefore receive any support from it.

There can hardly be any hope that by more accurate determinations of the atomic weights any essential addition will be made to our knowledge with respect to this ultimate matter. The next considerable

* W. Ostwald has arrived at the same conclusion by the theory of probabilities. See his *Lehrbuch der Allgemeinen Chemie*, 1884, vol. 1, pp 35, 119.

† M. Zängerle, "Ueber die Natur der Elemente, &c.," (*Programm des k. Realgymnasiums*, München, 1882.

‡ Edm. J. Mills, "On the Numerics of the Elements," *Phil. Mag.*, Nov., 1884, p. 393.

advance towards clearing this up would be the splitting up of an element into some homogeneous substance differing from the element from which it was obtained, as this might be either the ultimate matter itself or some condensation-product of it. Absolute certainty on this question, that is, the decomposition of all that are now considered to be elements into one and the same ultimate matter, is hardly to be expected.

From the atomic weight of silver, which has just been shown to have been most accurately determined, and from the weights of several other important elements* based on this determination, it necessarily follows that the atomic weight of silver, as well as of numerous other elements, confute Prout's hypothesis as originally adduced; it must, therefore, be regarded as experimentally disproved. The more recent forms of Prout's theory are, however, partly disproved by experiment, and partly are of such a nature as to be beyond experimental confirmation. They may therefore be classed as empty philosophical speculations, founded on a fundamental idea as to the unity of matter, about whose value and intrinsic probability no one will care to dispute†.

XLVIII.—*A New and Simple Method for the Quantitative Separation of Tellurium from Selenium.*

By EDWARD DIVERS, M.D., and MASACHIKA SHIMOSÉ, M.E., Imperial Japanese College of Engineering, Tôkio.

SELENIUM and tellurium are sharply distinguished from each other in their behaviour towards sulphur dioxide in the presence of sulphuric acid, and absence of hydrochloric acid. With precautions easy to be observed, the whole of the selenium is precipitated without a trace of the tellurium accompanying it. The sulphur dioxide solution must be added to the undiluted or very slightly diluted solution of the oxidised elements in concentrated sulphuric acid. Some dilution of the sulphuric acid is indeed necessary, as the precipitation of the selenium is incomplete without it, but this is most safely and simply effected by the sulphur dioxide solution itself. H. Rose has placed on record in the *Zeit. anal. Chem.*, 1, 73, his experience as to the imperfect precipitation of selenium by sulphur dioxide in presence of

* Compare the authors' "Table of Atomic Weights," corrected edition, Leipzig, 1884, by Breitkopf and Härtel.

† Compare Lothar Meyer, *Moderne Theorien*, 5th edition, p. 134.

sulphuric acid alone, but that is when it is dilute, and, in accordance with this, we find that the precipitation of selenium is not complete unless the sulphuric acid is sufficiently concentrated.

Carefully purified tellurium and selenium were employed in our last experiments, the former giving no trace of selenium to solution of potassium cyanide, and the latter entirely dissolving in this when warm. Weighed quantities were mixed for the trial, and after separation by the present method, were again weighed and tested by this reagent as to their purity. The quantities used and recovered in two experiments are here given. The accuracy of the method was further proved by qualitative testing.

	I.	II.
Tellurium taken	0·3115 grm. = 44·61 p. c.	0·2515 grm. = 42·55 p.c.
Selenium "	0·3867 " = 55·39 "	0·3395 " = 57·45 "
Tellurium found	0·3107* " = 44·50 "	0·2513 " = 42·52 "
Selenium "	0·3865 " = 55·35 "	0·3395 " = 57·45 "

The details of the method are as follows, taking the tellurium and selenium as in the free state. The mixture is heated with concentrated sulphuric acid in a covered beaker until it is entirely oxidised to a colourless solution with some white tellurium sulphate deposited. The heating may be continued to expel if necessary all traces of sulphur dioxide, as without doing this some precipitation of selenium will occur on diluting the solution with water—a matter of no consequence, however, when other insoluble substances are absent.

The solubility of the two substances in sulphuric acid before oxidation greatly aids this action, which, moreover, does not pass beyond the dioxide stage, a point material for the reduction that is to follow. Sulphuric acid is therefore decidedly preferable to nitric acid as the oxidising agent, although nitric acid may be used if desired; in this case the oxidation has to be followed by evaporation of the excess of nitric acid, heating with hydrochloric acid to reduce trioxides, and, lastly, heating with sulphuric acid to expel all hydrochloric acid.

A moderately strong solution of sulphur dioxide is then gradually added to the concentrated sulphuric acid solution until the volume is increased at least fivefold. This addition causes a continuous precipitation of red selenium until the dilution has gone far enough, which will not be before the volume has become about four times that of the sulphuric acid. The mixture is digested on the sand-bath for some time. The precipitate soon darkens in colour and becomes dense, without aggregating into masses difficult to wash, as it does in the ordinary method of heating with hydrochloric acid. After

* This analysis was complicated by the filter breaking.

diluting a little more, to make the filter safe, the precipitate is washed and dried on a tared filter and weighed. It may finally be tested for tellurium.

The filtrate is heated with hydrochloric acid and more sulphur dioxide so as to precipitate the tellurium in the usual way. It may be tested for selenium, and the mother-liquor treated with hydrogen sulphide to prove that it is free from both elements.

It will be seen that the method here described is much more simple than the cyanide method. Besides those well known, another complication has already been pointed out by one of us (*Chem. News*, 49, 27),* due to hot solution of cyanide dissolving a little tellurium that is precipitable by hydrochloric acid, in addition to that thrown down by sulphur dioxide after the action of hydrochloric acid is over.

XLIX.—*Reactions of Selenious Acid with Hydrogen Sulphide, and of Sulphurous Acid with Hydrogen Selenide.*

By EDWARD DIVERS, M.D., and TETSUKICHI SHIMIDZU, M.E., Imperial Japanese College of Engineering, Tôkiô.

THE nature of the reaction of hydrogen sulphide with selenious acid, and of that of hydrogen selenide with sulphurous acid, is evidently of special interest on account of the close similarity of sulphur and selenium, and many chemists—Berzelius, Rose, Rathke, Bettendorff, Ditté, v. Gerichten—have been led to study it in consequence. We have just completed a simple investigation of these reactions, and have observed some new facts of interest, which not only supplement what is already known concerning them, but also appear to us to place their nature in a clearer light than that in which it has hitherto stood.

Hydrogen Sulphide and Selenious Acid react together in two ways.

A very cold dilute solution of selenious acid yields a precipitate with hydrogen sulphide, composed of two atoms of sulphur to one of selenium, and which is yellow and pulverulent. This is well known, and also that in warmer solutions the precipitate becomes plastic and

* Since this fact was communicated to the *Chemical News*, we have found that H. Rose had observed the same thing, and mentioned it in his "Quantitative Analysis," but it seems to be one little known, and *tellurocyanates* are treated as having no existence.

red. But when the solution is warm another reaction also takes place, which appears to have as yet escaped all notice. In this case, namely, *sulphuric acid is formed, and the precipitate does not now contain so much as two atoms of sulphur to one of selenium.*

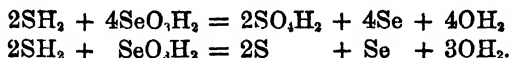
Selenious acid, therefore, exerts an oxidising action not only on the hydrogen, but also on the sulphur of the hydrogen sulphide. This action always occurs to a sufficient extent to allow of the sulphuric acid being detected, except when the solutions are cold in the cold season of the year, and should, therefore, be taken into consideration in analytical work. In hot solutions, it is very extensive. Thus, in one trial we got nearly one-fourth of the oxygen of the selenium dioxide in the form of sulphuric acid, SO_4H_2 . Here we kept the solution boiling, and allowed the gaseous hydrogen sulphide to flow upon its surface only. In another trial, in which we bubbled the gas through a hot solution, we obtained nearly one-sixth of the oxygen as sulphuric acid. The precipitates produced in these trials were analysed and found to contain, in the former case scarcely more than two-fifths of an atom of sulphur to one of selenium, and in the latter case only two-thirds of an atom of sulphur to one of selenium.

These quantities of precipitated sulphur are, however, very far from representing all the unoxidised sulphur, as this escaped in abundance with the steam and excess of gas. By calculation, indeed, more than one atom of sulphur must thus have volatilised to every atom of selenium precipitated from the boiling solution, and just about one atom to one of precipitated selenium from the merely hot solution. Although the evolved vapour was quite clear, the condensed water contained much milky sulphur, and believing that this sulphur might come from a reaction between sulphur dioxide and hydrogen sulphide gases, because the extent of the volatilisation of sulphur so far exceeded that which occurs when sulphur in powder is boiled with water, we tested, first, the steam with no result, and then the action of hydrogen sulphide on a hot concentrated solution of ferric chloride, which we found to give a similarly abundant volatilisation of sulphur. We also tested our mother-liquors from the precipitates for other sulphur acids, but found nothing except sulphuric acid. The presence of hydrochloric acid during precipitation seemed to have no effect beyond that of causing the precipitate to aggregate and settle.

The selenious acid used in our experiments was prepared in our College Laboratory from selenium free from sulphur or tellurium, and almost pure, and was repeatedly evaporated to dryness with hydrochloric acid, and heated to the subliming point.

On consideration, it will be seen that since selenious acid so readily oxidises sulphurous acid, the fact of its completely oxidising hydrogen sulphide under favourable circumstances is only what might have

been expected. In exerting this action, four times as much selenium is precipitated from it as when only the hydrogen of the same quantity of sulphide is attacked by it, as may be seen from the equations—



Sulphurous Acid with Hydrogen Selenide in Excess yields Selenium, Water, and Hydrogen Sulphide.

On adding a weak solution of sulphur dioxide to a strong solution of hydrogen selenide, gradually and with agitation, so as to leave some hydrogen selenide undecomposed, *selenium alone is precipitated*, quite free from sulphur, and of a fine deep-red colour from the first and for some time after; it ultimately becomes brown-red, however, if hydrogen selenide is kept in contact with it. *The mother-liquor contains hydrogen sulphide* along with any remaining hydrogen selenide.

When, on the other hand, gaseous hydrogen selenide is passed into sulphur dioxide solution, an orange-red precipitate is produced which contains sulphur. A precipitate thus generated in a mother-liquor in which a little sulphur dioxide was purposely left undecomposed, was analysed and found to contain only one—strictly 0·95—atom of sulphur to two of selenium. In another experiment in which no sulphur dioxide was left unchanged, the mother-liquor contained a very little selenium, even after boiling; this only slowly yielded a black precipitate of silver selenide with silver nitrate. We conclude from this that it contained a seleniothionic acid, perhaps one of those already known.

We do not at once discuss the nature of the reaction between hydrogen selenide and sulphurous acid, and of the secondary reactions which may accompany it, because we have yet to describe, in a later section of this paper, experiments which throw further light on what happens when the two substances come together.

Iron Monoselenide, and the Preparation of Hydrogen Selenide from it.

In preparing the hydrogen selenide required we imitated the common process of preparing hydrogen sulphide. An iron selenide was first made by projecting into a black-lead pot, heated in a wind-furnace, a mixture of wrought-iron filings and selenium. In this operation most of the selenium was dissipated in vapour. When the iron had grown hot more selenium was added which combined with the iron with very little loss, causing vivid ignition and complete liquefaction of the whole. The fluid compound was run into a mould

and cooled. The solid mass thus obtained was indistinguishable in appearance from iron sulphide similarly prepared.

Not being very sensitive to the action of acids, it was powdered before being put in the apparatus for generating the gas, and then warmed with dilute hydrochloric acid. This gave a steady stream of gas.

The iron selenide proved on analysis to be a compound of almost exactly one atom of selenium with one of iron. It was, therefore, iron monoselenide. Like artificial iron sulphide it was, nevertheless, impure, although only slightly so. For, on the one hand, the gas evolved on treating it with hydrochloric acid contained a very small fraction of its volume of free hydrogen, and, on the other, a very small but voluminous black residue was left insoluble in the acid; this contained selenium, and was doubtless iron biselenide. Our preparation, consequently, contained both a little free iron and a little biselenide intermixed with the monoselenide. This is the first time iron monoselenide has been obtained.

Sulphur Decomposes Hydrogen Selenide.

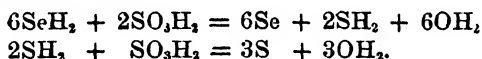
A solution of hydrogen selenide is very much more sensitive to the action of air than one of hydrogen sulphide, and quickly becomes red on the surface after a very short exposure. As oxygen precipitates selenium so readily from its hydride, sulphur may be expected to do the same, although less actively, and our experiments have shown us that sulphur has this action, and even appears to exert it as freely as oxygen. As flowers of sulphur usually contain some sulphurous acid, we employed only roll-sulphur in our experiments. On adding this to a solution of hydrogen selenide, or on bubbling hydrogen selenide through water containing it in lumps or in powder, it instantly becomes coloured by precipitated selenium, at first orange-red, then deep red, and, lastly, but only by the prolonged action of the gas, dark brown-red. The action of the hydrogen selenide on the sulphur is, however, quite superficial; so that much of it is required to decompose completely a little hydrogen selenide. Simultaneously with the deposition of the selenium, *hydrogen sulphide is formed*. This being so readily carried away by the current of hydrogen selenide gas, it is better, in order to detect it, to digest the sulphur in a closed bottle with hydrogen selenide solution, add some hydrochloric acid to aggregate and separate suspended selenium, and then quickly filter with but little exposure to the air. The mother-liquor thus obtained and deprived of all hydrogen selenide will furnish ample evidence of the formation of hydrogen sulphide.*

* Hydrogen selenide quickly permeates black vulcanised rubber tubing, turning it red and, no doubt, by the above reaction with the sulphur in it.

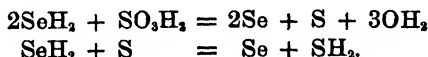
The sulphur with its deposited selenium, dried and heated in a vacuum, gave off no gas, so that the deposit contains no hydrogen persulphide or perselenide. The cause of the brown-red instead of bright red colour of the deposit remained unexplained. It can be produced in pure bright red selenium by digesting it in hydrogen selenide solution.

Having established the occurrence of a reaction between sulphur and hydrogen selenide, we tried whether we could not get selenium free from sulphur by treating the orange-red precipitate which is produced when sulphurous acid is first acted on by hydrogen selenide with an excess of the last-named substance. By this treatment the colour of the precipitate changed to deep red, ultimately to brown-red, and on examination it was found to contain only traces of sulphur. In performing this experiment, we took the precaution, in order to avoid any consolidation of the precipitate, to work with it freshly prepared and suspended in very cold water. We are now in a better position than we were to consider the nature of the reaction between hydrogen selenide and sulphurous acid.

Hydrogen selenide in excess yielding with sulphurous acid both hydrogen sulphide and a precipitate wholly selenium, the presence of sulphur in the precipitate, when the sulphurous acid has been kept in excess, might be attributed to the interaction of hydrogen sulphide and sulphurous acid, thus :—



These reactions combined give the 2Se to 1S found by us, and recognised in books as sulphur biselenide. But if they represent the true order of events, some pentathionic acid should be formed, whereas, in the mother-liquor we found none ; but, instead, a little seleniothionic acid. It is, besides, certain that in the reduction of sulphur dioxide the oxygen will be before the sulphur in taking hydrogen, and that thus nascent sulphur will be in presence of hydrogen selenide, with which it must react. The order of the changes will therefore be represented more correctly by the following equations than by those above set out :—



Our finding a little less than one atom of sulphur to two of selenium is thus accounted for by some action under the circumstances between the sulphur precipitated and the hydrogen selenide ; whilst the absence of pentathionic acid no longer remains a difficulty, and the presence of a little seleniothionic acid becomes an occurrence to be expected.

The only Compound of Sulphur and Selenium known as yet is Selenium Monosulphide.

In so far as it is possible to prepare by definite reactions precipitates having, in one case, the composition of selenium bisulphide and, in the other case, of sulphur biselenide, such precipitates may be these respective compounds. Chemists are not agreed that they are, but in systematic treatises on chemistry it is not uncommon to find them so represented. We ourselves consider, irrespectively of any facts bearing upon the point which our work adds to those already known, that there is no evidence that they are; and that it is theoretically improbable that sulphur biselenide should exist at all.

The precipitate at first obtained from selenious acid is lemon-yellow, and that from sulphurous acid orange-red, and Ditté has shown that, on leaving the former for some time moistened with carbon bisulphide, it becomes converted into transparent, orange-yellow scales, having very accurately the composition of selenium monosulphide. The excess of sulphur in the original precipitate goes into solution in the carbon bisulphide. By taking, in place of selenious acid, a neutral selenite solution for precipitation, this sulphide can be more readily obtained in the subsequent treatment with carbon bisulphide, but it is then of a dark brown-red colour.*

This substance, as prepared by Ditté in apparently two forms, one approaching sulphur in colour, and the other selenium, is not only of constant and simple atomic composition, but it has a density markedly less than that calculated for it from the densities and proportions of its components, and disengages during oxidation much more heat than its components would if uncombined. Ditté places it, therefore, among "explosive" compounds. It is an exceedingly unstable body.

The existence of selenium monosulphide, SeS , has, therefore, long been incontestably proved (unless Ditté's facts are disputed), although it has not received that general recognition which it deserves.

Precipitates of sulphur with selenium have no other properties than those of mixtures of these simple substances.†

* This colour Ditté attributes to some action of alkali hydrosulphide that becomes formed during the precipitation, and it has already been mentioned by us, in a previous section of this paper, that the same colour is produced in selenium precipitated by sulphur, when this is long digested with hydrogen selenide solution, and, further, that pure selenium, precipitated from hydrogen selenide by sulphurous acid not in excess, ultimately takes this colour, provided it is kept in hydrogen selenide solution for some time, although otherwise it preserves its brilliant, deep red colour.

† The deep red colour of unmixed precipitated selenium and the orange-red colour of some of its precipitates with sulphur, are well matched by the deep red of ordinary amorphous phosphorus, and the orange-red of this substance when formed during the partial combustion of ordinary crystalline phosphorus.

We have already described in this paper the copious volatilisation of sulphur which takes place when precipitation takes place in hot solutions, and wish now to point out that, since in precipitating any true metal sulphide from a hot solution, no such volatilisation of sulphur occurs, even in the case of tellurium sulphide, it affords proof that the nascent sulphur is uncombined with the selenium when precipitated along with it.

It is usual to regard the reactions of which we are now treating, as cases of double decomposition, but considering how very similar sulphur and selenium are, the propriety of doing so may well be doubted. The reactions will be sufficiently determined solely by the property possessed by the hydrogen and oxygen of combining together, and the atoms of sulphur and selenium will then be left to unite, each kind together, or in part with the other kind to form selenium monosulphide.

Moreover, it seems like a reversal of the well-established electro-chemical order of the elements to admit that selenium can be at one time basylous and at another chlorous to sulphur under very similar conditions. Yet this would be the case if we admit the formation of a sulphur selenide by double decomposition. Were there indeed facts to prove this formation, the force of the objection to it that it is improbable, would not count for much, and it is brought forward here merely to combat the accepted notions of what ought to be the nature of the reactions by showing that analogy gives no support to these views any more than do the facts known concerning the reactions.

Conclusions.

Hydrogen sulphide and selenious acid, and also hydrogen selenide and sulphurous acid, yield a precipitate of sulphur and selenium, which consists of two atoms of sulphur to one of selenium in the former case, and of one atom of sulphur to two atoms of selenium in the latter, for the most part uncombined in both cases.

Hydrogen sulphide and selenious acid also react freely in hot solutions in another way, and then form sulphuric acid and selenium.

Hydrogen selenide and sulphur in contact change at once into hydrogen sulphide and selenium. Accordingly, hydrogen selenide in excess gives with sulphurous acid a precipitate of pure selenium.

What is known concerning the precipitation of sulphur along with selenium furnishes no grounds for admitting the existence of any compound of the two elements other than the very unstable selenium monosulphide described by Ditté in 1871.

LI.—Researches on the Action of the Copper-zinc Couple on Organic Bodies. Part X. On Bromide of Benzyl.

By J. H. GLADSTONE, Ph.D., F.R.S., and ALFRED TRIBE, F.C.S.,
Lecturer on Metallurgy to the Medical School of the National
Dental Hospital.

OUR previous researches on the action of the copper-zinc couple on organic bodies of the fatty acid series enabled us to prepare several organo-zinc compounds and paraffins. We have since extended the investigation to compounds of the aromatic series, in the hope especially of preparing some organo-zinc body belonging to the phenyl group.

The existence of three isomeric bodies having the ultimate composition C_7H_7Br , namely, ortho- and para-bromotoluene and benzyl bromide, attracted our attention, especially as we thought it might be possible to throw some further light on the difference in their structure. On trying the experiment, it was found that neither ortho- nor para-bromotoluene was acted on by the copper-zinc couple either alone or in the presence of alcohol or ether. Benzyl bromide, on the contrary, was acted on by the copper-zinc couple very readily. When about 10 c.c. of the liquid were poured upon 10 grams of the couple, the bromide slowly became darker in colour, and presently fumes of hydrobromic acid were evolved. When, however, the materials were brought together in larger proportion, 100 c.c. of the bromide to 50 grams of the couple, hydrobromic acid was evolved almost immediately, the temperature rose very rapidly, and the action became explosive in character. The experiments, therefore, had to be made on comparatively small quantities. In one experiment 10 c.c. (14.3 grams) were poured upon 10 grams of the dry couple in a flask to which an inverted condenser was attached. The flask was placed in boiling water, when fumes of hydrobromic acid were copiously evolved; a violent frothing occurred in about an hour, and in two hours from the commencement of heating the action practically ceased; the dark brown mass found in the flask mixed with residual couple was treated with ether, in which it partly dissolved, the residue being soluble in benzene.

The ethereal solution contained an organic body and zinc bromide, which was separated from it by means of water, and was found to weigh 1.91 grams. The carbon compound, purified by being redissolved in ether and precipitated by water, was found to weigh

5.15 grams. It was a yellowish-red substance, resembled resin, melted at 42° , and distilled at near redness with a considerable amount of charring and decomposition. It had a faint odour suggesting that of honey. It dissolved in ether, as already stated, very sparingly in alcohol, and readily in benzene.

On combustion with copper oxide and chromate of lead, this resin-like body gave the following percentages of carbon and hydrogen:—

	I.	II.	III.	Mean.
Carbon	92.91	92.75	93.12	92.93
Hydrogen	6.87	6.96	6.88	6.90
	99.78	99.71	100.00	99.83

The body before mentioned as insoluble in ether, but soluble in benzene, was found to consist of a brownish resinoid substance, weighing 2.46 grams; it did not dissolve either in alcohol or in ether, unless to a very small extent; it contained no zinc compound, and only a little bromine. On combustion, it gave the following percentages:—

	I.	II.	III.	Mean.
Carbon	92.14	92.19	92.01	92.10
Hydrogen	6.59	6.93	6.63	6.72
	98.73	99.12	98.64	98.82

Making allowance for the 1 or 2 per cent. of brominated compound in the second substance, these two different bodies are evidently hydrocarbons, identical, or nearly so, in composition. We are disposed to regard them both as isomerides or polymerides of the composition C_7H_8 , which would require the percentages of—

Carbon	93.33
Hydrogen	6.67
	100.00

This is almost exactly the proportion of the carbon and hydrogen in the second resin, but the first contains a slight excess of hydrogen, which may possibly be due to a little dibenzyl. A substance of the composition $C_{10}H_{12}$ would have given 7.69 per cent. of hydrogen.

A solution of the first body in benzene was examined as to its optical properties, and it was found that the specific refraction of the substance was 0.5761 for the line A, and 0.6091 for the line F. These figures are higher than those of bodies of the C_nH_n type, and support the view that the resin consists, mainly, of some body containing a larger proportion of carbon.

A very similar result was obtained when the body insoluble in ether was purified by alcohol from the brominated compound and examined optically.

That there was no complete breaking down of the aromatic compound during the violent reaction is pretty evident from the amount of the resinous bodies obtained, $5.15 + 2.46 = 7.61$ grams. The theoretical amount of C_7H_6 obtainable from the original 14.3 grams of C_7H_7Br is 7.52 grams.

It appears, therefore, that by the action of the copper-zinc couple C_7H_7Br is split up into $HBr + C_7H_6$. By what intermediate steps this may take place, we have had no means of judging. The formation of zinc bromide suggests the simultaneous production of dibenzyl, $C_{12}H_{14}$. It is not difficult, however, to account for the formation of zinc bromide otherwise, seeing that we had zinc in juxtaposition with hydrobromic acid.

This C_7H_6 or $(C_7H_6)_n$ is not stilbene. Its non-crystalline character, its melting point, and its optical properties all demonstrate that. Its physical properties also distinguish it from the isomeric di-hydroanthracene and isostilbene. We propose calling it *benzylene*, a name formerly given by Wicke to his hypothetical radicle C_7H_5 , and to distinguish the substance soluble in ether as α -benzylene, and that insoluble in ether as β -benzylene.

The behaviour of these two modifications with ether was closely studied under the microscope. Both of them are very brittle solids at the ordinary temperature, translucent, with a conchoidal fracture. The α -modification absorbs the vapour of ether very readily, and when treated with liquid ether the solid pieces immediately lose their form, swell, and run down into a viscid liquid, through which rise a quantity of bubbles. At the same time, some of the compound is dissolved by the ether, and separates in myriads of minute globules on spontaneous evaporation of the solvent. The specimen of the β -modification already described, showed the same properties to a smaller degree, but as it doubtless contained some of the more soluble body, a portion of it was dissolved in a little benzene and treated with a considerable quantity of ether. This produced a milky liquid from which a viscid body subsided. When dried, this became brittle, and was found no longer to absorb the vapour of ether, or to dissolve to an appreciable extent in that solvent. It dissolved very readily in benzene or chloroform. It began to soften at about 120° , becoming at a higher temperature a dark liquid which seems not to distil without decomposition. The specific refraction of this body, dissolved in benzene, was found to be 0.5664 for the line A, and 0.6016 for the line F (difference 0.0352), which confirms the composition $(C_7H_6)_n$ previously attributed to it. The force of this deduction from the

optical properties lies in the fact that the specific refraction of a body of the composition C_nH_n , rarely, if ever, exceeds 0.5600 for the line A, and 0.5850 for the line F, the difference being 0.0250; while all hydrocarbons in which the atoms of carbon are in excess of those of hydrogen have a higher specific refraction, and a difference between A and F of at least 0.0360.*

An experiment was made with 10 c.c. (11.03 grams) of benzyl chloride instead of bromide, poured on to 10 grams of couple. There was little or no action at the ordinary temperature for 24 hours. When heated to 70°, the action commenced with the evolution of hydrochloric acid, which for about two hours continued at a temperature of 100°. The product, dissolved in ether and treated as before, was found to consist of 1.31 grams of zinc chloride and 5.4 grams of a viscid, resin-like body. The portion insoluble in ether, when treated with benzene, gave 0.36 gram of resinous matter. The viscid body was of a reddish-brown colour, with blue fluorescence. It became liquid at 35°, at which temperature its sp. gr. was 1.106, and its spec. ref. 0.563 for A and 0.594 for F. On combustion, it gave the following results:—

	I.	II.
Carbon	91.31	90.80
Hydrogen	6.99	6.90
	<hr/> 98.30	<hr/> 97.70

It had an odour resembling that of honey; and was very readily soluble in ether. When strongly treated *per se*, it was decomposed, giving the same remarkable odour as was obtained on the distillation of the resinous bodies previously examined. It was evidently an impure specimen of benzylene. The action with the chloride was therefore analogous to that with the bromide; but there was a larger amount of bye-products.

As this benzylene is a non-saturated hydrocarbon, it was to be expected that substitution products would be easily formed from it. On treating with strong nitric acid, a nitro-compound is produced. It did not show the slightest power of crystallising. It melts easily, and at a higher temperature explodes, with the production of a great deal of carbon; it is fairly soluble in benzene or ether, and sparingly soluble in alcohol or bisulphide of carbon; it separates from all these solutions in a liquid condition at the ordinary temperature, but solidifies on standing.

* Most of these properties of the purified β -benzylene have been added since the paper was read at the Society.

Action in Presence of Ether.

The action of the copper-zinc couple on benzyl bromide in presence of ether is very energetic, but the nature of it differs entirely from that of the couple on the compound alone. Hydrobromic acid is not evolved, nor did we find any resinous compound. Thus, when 5 c.c. (7.15 grams) of the bromide were mixed with 10 c.c. of anhydrous ether, and the mixture was added to 10 grams of the couple in a flask fitted with an inverted condenser, the temperature of the liquid quickly increased, and, though the flask was immersed in cold water, the action was over in five minutes. The solution in the flask was miscible in absolute alcohol in all proportions. When water was added either to the ethereal solution, or to the ethereal solution containing alcohol, zinc hydrate was formed, equivalent to 0.632 gram ZnO .

It is well known that water precipitates zinc hydrate from an ethereal solution of the $\text{C}_n\text{H}_{2n+1}\text{IZn}$ compounds, with the formation of the corresponding paraffin. The precipitation of zinc hydrate therefore from the ethereal solution in the above experiment naturally suggested the presence of a benzyl compound of analogous composition, that is to say, zinc bromo-benzide, $\text{C}_7\text{H}_7\text{BrZn}$. But if this be true, analogy requires that, simultaneously with the precipitation of the zinc hydrate, there should be formed a hydrocarbon, C_7H_8 . In order to obtain conclusive evidence of the presence of this in the oily fluid referred to above, it was necessary to experiment on a larger scale. Accordingly 100 c.c. of benzyl bromide were similarly decomposed in small quantities at a time; to the joint product, water was added, and just enough hydrochloric acid to dissolve the precipitated zinc hydrate. The oily liquid which separated was washed two or three times with water, and fractionally distilled. It commenced to boil at about 40° , the thermometer rose to 280° , when a distillate was obtained which solidified in the receiver. The temperature in a little time rose beyond the limits of the thermometer, and a small quantity of a brown tarry substance distilled. By repeated fractional distillation two compounds were isolated besides this tarry body.

The first of these compounds consisted of about 20 c.c. of a very mobile liquid, which was not acted on by sodium, and had the odour of toluene. Its physical properties, as shown below, were practically identical with those of that substance, as determined from a specimen which was reputed to be chemically pure:—

Physical properties.*	Of mobile liquid.	Of pure toluene.
Boiling point	108° to 111° C.	110° to 111° C.
Specific gravity at 14°	0·8691	0·8643
Refractive index (for A) at 14°	1·4883	1·4855
Specific refraction	0·5618	0·5617
Specific dispersion	0·0464	0·0462

There seems no need of further proof that this liquid was *toluene*.

The second compound solidified, as the liquid cooled, to a mass of crystals consisting of broken prisms. It readily dissolved in hot alcohol, from which it separated on cooling, and after three or four crystallisations the crystals had the form of rhomboidal plates. On combustion with oxide of copper it gave numbers agreeing with the formula $C_{14}H_{14}$, thus:—

	Found.	Calculated.
Carbon	91·92	92·31
Hydrogen	7·85	7·69
	99·77	100·00

The specific refraction of this substance dissolved in benzene was 0·5580 for A, with a specific dispersion of 0·0440, which is in perfect accordance with the optical properties of a body of the composition C_nH_n . All these properties show that it is the known substance *dibenzyl*.

As we observed some years ago that the yield of zinc iodo-amylate depended very much on the temperature during the reaction, the experiment above described was repeated with modifications of temperature, in the hope of obtaining a larger proportion of the supposed organo-zinc body. The ratio between the bromine and the zinc in the resulting solution was determined as follows:—

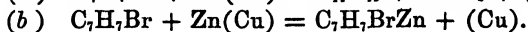
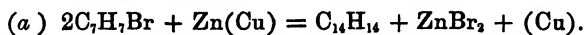
Experiment.	Atomic ratio in result. Zinc : bromine.
(1.) Flask in boiling water	1 : 1·593
(2.) Flask cooled by occasional immersion in cold water	1 : 1·600
(3.) Flask in ice-cold water	1 : 1·578

The relative amount therefore was practically the same in all three cases.

* The sp. gr. is compared with water at 4°; the specific refraction is calculated for the line A of the spectrum; the specific dispersion is the difference of the specific refractions for the lines A and H.

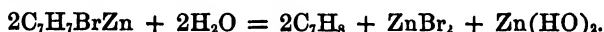
The results above described would appear to justify the following conclusions:—

(1.) That the action of the copper-zinc couple on an ethereal solution of benzyl bromide produces dibenzyl, zinc bromide, and zinc bromo-benzide, according to the following equations:—



If the action were to take place exactly in the proportions of these two equations, the atomic ratio of zinc to bromine would obviously be 1 : 1.5. It appears, however, that the action takes place very nearly in the proportion of three of equation (a) to two of equation (b).

(2) That the action of water on zinc bromo-benzide produces zinc hydrate, zinc bromide, and toluene, thus:—



In order to satisfy ourselves that toluene was really produced by the action of the water, and in the hope of perhaps being able to effect the isolation of the zinc benzide, we acted on another 100 c.c. of benzyl bromide mixed with ether. The product was separated by filtration from the excess of couple, and distilled by heating in a bath up to 130° until the liquid ceased to come over. This portion was found to consist of ether, with a very small amount of the products of the reaction. When the distillation at this temperature had ceased, a brown viscous mass was noticed in the flask, apparently insoluble in the remaining liquid. This liquid was removed into a retort, and distilled over a lamp; an almost colourless liquid was obtained, followed by some brown tarry matters. The colourless liquid on rectification was found to consist mainly of dibenzyl dissolved in a small quantity of a liquid which boiled at a lower temperature. This liquid apparently contained traces of toluene, together with some liquid of a higher boiling point. This was found to have a sp gr. considerably above that of water, with a comparatively low specific refraction, whilst its specific dispersion indicated that we were still dealing with bodies in which six atoms of carbon are "doubly-linked." These properties raised a suspicion that the liquid was a bromine compound. When some of it was dissolved in toluene, and heated with metallic sodium, decomposition ensued with separation of carbon, and a large amount of sodium bromide was formed. The amount of this brominated compound obtained was too small for purification, and we have not been able to satisfy ourselves whether it is the same substance which has been noticed in some of the products of this reaction, a substance having a pungent odour, and causing an unpleasant sensation in the throat, but not a flow of tears as the

original bromide does. The brown viscous mass left in the flask was further distilled, but no volatile zinc compound was obtained. The ratio of zinc to bromine in it was, however, determined and found to be as 1 : 1.6, as in the previous experiments.

It would appear, therefore, that the principal organic product of this reaction is dibenzyl, formed by the direct removal of the bromine by the zinc, and partly perhaps by the destructive distillation of a bromo-zinc compound first produced.

It was found that when the products of the reaction above described were treated with two or three times their volume of anhydrous ether, a white solid substance separated. This was readily soluble in absolute alcohol; it contained both zinc and bromine. Attempts were made to analyse it, but without much success, on account of its tendency to change into another substance insoluble in alcohol; but in one case where it was washed several times with ether by decantation, the ratio of zinc to bromine was determined as 3 : 2.

Action in Presence of Alcohol.

As the zinc compound produced in the reaction in presence of ether was not decomposed by alcohol, but was broken up by water, it became necessary to see what was the action of the couple on benzyl bromide in presence of alcohol itself. The nature of the reaction was found to be very different.

In an experiment, 5 c.c. of the bromide and 10 c.c. of absolute alcohol were poured on to 10 grams of copper-zinc couple. The temperature of the liquid rose almost immediately; in three minutes it boiled, and in two more the action practically ceased. The liquid in the flask was somewhat viscous and almost colourless. The addition of water to it produced a copious separation of zinc hydrate, and on analysis it was found to contain zinc and bromine in the atomic proportions of 1 : 1.15. This near equality in the proportions of the elements shows that the action differs from what takes place in presence of ether, and suggests that it consists in the formation either of the supposed zinc bromo-benzide, or of the known zinc bromethylate, or possibly of a mixture of these bodies. The atomic proportion of zinc and bromine in either of these compounds would be 1 : 1. Supposing the action to be similar to what takes place in the fatty acid series of bodies, with the production of bromethylate of zinc, C_7H_5 would be formed thus: $-C_7H_7Br + C_2H_5O + Zn(Cu) = C_7H_5 + ZnC_2H_5OBr + (Cu)$. Supposing, on the contrary, that the bromide of benzyl simply combines with an atom of zinc, there will be no hydrocarbon separated.

In order to ascertain whether toluene was a product of this reaction, 20 c.c. of the bromide, mixed with 40 c.c. of absolute alcohol,

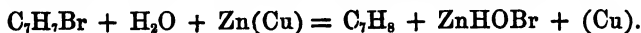
were acted on by the couple as before. The liquid was poured off the residual couple and distilled up to a temperature of 130° . On redistillation nearly the whole of this portion passed over at the temperature at which alcohol boils (78°), but on examining it in a hollow prism, it was at once seen to be far from pure alcohol. Indeed the increased refraction and dispersion led to the belief that one-fifth of it was toluene. On the addition of water 6—8 c.c. of a clear liquid separated, which redistilled at about 111° , had a sp. gr. of 0.8610, with a specific refraction of 0.5604, and a specific dispersion of 0.0474. It was therefore pretty pure toluene. On heating the residuum in the flask at above 130° , a coloured liquid was obtained in which some dibenzyl was detected. We conclude, therefore, that the main action is that expressed by the above equation, whilst our experiments do not enable us to decide as to the presence or absence of any zinc bromo-benzide among the products.

Action in Presence of Water.

When benzyl bromide was added to a wet couple made with granulated zinc, the temperature rose slowly, and in 24 hours the action was found to be complete, with crystals of dibenzyl visible on the residual mass. The flask was then immersed in a paraffin-bath at 130° . The distillate consisted of water, a comparatively small quantity of a liquid with the specific gravity, refraction, and dispersion of toluene, and a little dibenzyl. The flask contained more dibenzyl and a small quantity of a brown resinous substance. We conclude that the action of the couple on benzyl bromide in presence of water is for the most part represented by the following equation:—



while at the same time a portion is decomposed as follows:—



The above research is not so complete as we could wish; but the highly painful and injurious character of the vapour of benzyl bromide, even in the smallest quantities, deterred us from continuing its examination. We believe that we have established, at any rate, some points of analogy between the action of the copper-zinc couple on members of the fatty acid and on the aromatic series, and have indicated the existence of some new compounds.

LI. — *On the Existence of Nitrous Anhydride in the Gaseous State.*

By G. LUNGE.

THE above question has been several times investigated, and I have myself published a number of papers on this subject.* What induces me to return to it is a communication to this Society by Ramsay and Cundall (this vol., 187—198). These chemists deny the existence of nitrous anhydride, N_2O_3 , in the gaseous state, but they assume it to exist in the blue or green liquid obtained at a low temperature. In discussing this paper (*Abstracts of the Proceedings*, No. 3, p. 23), Armstrong goes even further by saying: "The method adopted by the authors did not suffice to prove the existence of N_2O_3 , even as a liquid, and their results could be equally well interpreted on the assumption that they were dealing with a solution of NO in N_2O_4 ."

I, for my part, have always felt myself compelled to defend the contrary opinion, *i.e.*, that N_2O_3 exists not merely in the liquid state, but also as a vapour or gas. The reasons given for my opinion are recorded in my previous papers, and will be partly mentioned in the present communication also. If Ramsay and Cundall had refuted them, the matter would rest as they left it. But those authors, although they mention my papers, have paid scarcely any attention to them, and even the little they quote of my results is erroneous. The argument upon which I insisted as the principal one, and which as yet has never been refuted, they do not mention at all.

The reason why I lay stress upon recording my dissent from the opinion held by Ramsay and Cundall, that N_2O_3 does not exist in the gaseous state, is that it clashes with the theory of the vitriol-chamber process, which I have been led to adopt as the only one compatible with a large number of ascertained facts. The immense importance of the process of manufacturing sulphuric acid is my apology for continuing this controversy.

Ramsay and Cundall prepare the material they work on by the action of nitric acid on arsenious anhydride. But they seem to be unaware of the previous researches on the influence which the *concentration* of the nitric acid employed exerts on the composition of the nitrogen oxides produced. I have myself shown, by a number of experiments,† what is the composition of the products obtained with

* See especially *Ber.*, 11, 1232; 12, 357; 15, 495; *Dingl. polyt. J.*, 233, 68.

† *Ber.*, 11, 1641. This paper is quoted, amongst others, by Ramsay and Cundall, but no notice is taken of its contents. [Stenhouse and Groves in 1877 (this *Jour.*, 1877, i, 545) called attention to the effect both of the temperature and of the concentration of the acid on the nature of the gases evolved: they recommend nitric acid of sp. gr. 1·30—1·31, and a temperature of 70° as giving the best result.—EDITOR.]

acids of different degrees of concentration. More especially I have shown that, when nitric acid of greater sp. gr. than 1.35 is employed, large quantities of N_2O_3 are produced along with N_2O_4 , whereas acid of sp. gr. 1.5 produces a gas, composed nine-tenths of N_2O_4 and one-tenth of N_2O_3 . I have also shown* that the blue liquid condensed from the purest N_2O_3 , even when rectified several times over, still contains a little N_2O_4 , because N_2O_3 , on vaporisation, is *partially* dissociated, and NO escapes. Ramsay and Cundall, notwithstanding this, say (p. 187): "It is commonly believed that the indigo-blue or green liquid produced by the action of arsenious anhydride on nitric acid has the formula N_2O_3 ," thus ignoring my previous researches quoted by themselves. They work with nitric acid of sp. gr. 1.5, sometimes even adding strong sulphuric acid, and employ the product as a starting point for an investigation of the behaviour of the compound N_2O_3 , whilst they might have learned from my research that their substance would not consist of N_2O_3 , but principally of N_2O_4 . This is indeed evident from their own analyses. Their results vary from 28.5 to 30.4 per cent. of nitrogen, whereas N_2O_3 requires 36.84 N, N_2O_4 30.48 N. The products analysed by them had an indigo-green, olive-green, or red colour. Their own analyses would seem to show that they had obtained no N_2O_3 whatever, and looking at these I cannot understand why they found merely sometimes, but not always, the reddish-yellow colour characteristic of N_2O_4 . In a few cases, they subsequently modify the product by passing NO through or over it, but even then they do not get beyond 31.56 per cent. of nitrogen, and even by mixing the vapour with excess of NO, and condensing the product at -20° to -25° , they merely get up to 32.44 per cent. N, thus obtaining, according to their own calculation, a mixture of 31.3 parts N_2O_3 with 68.7 parts N_2O_4 . Experiments made with such material cannot claim any considerable value for deciding the question in point, since I have shown how easy it is to obtain liquids composed almost entirely of N_2O_3 .

Their analytical methods also exhibit too little regard for previous publications. Their first plan consists in placing the substance, sealed in glass bulbs, in stoppered bottles containing very dilute solution of caustic soda, breaking the bulb by shaking the bottle and titrating the uncombined soda with standard acid. They themselves notice that this process is inaccurate, probably on account of NO being formed. But this had been known long ago, and had been pointed out by myself several times;† even when the titration is

* *Dingl. polyt. J.*, 233, 68. This is a detailed description of my research, to which attention had been drawn in the short summary published in *Ber.*, 12, 357.

† Especially *Ber.*, 10, 1076, and *Dingl. polyt. J.*, 228, 155.

replaced by an actual estimation of the nitrogen present in the alkaline liquid, the source of error just mentioned must remain.

After this they try some other methods, for some time without success. Amongst these they mention estimating the nitrous acid by means of standard potassium permanganate; this they found to be unsatisfactory "on account of the inconvenient and tedious time-reactions which take place." Since they tried this process with "the neutralised solutions of the previous process," *i.e.*, with such in which they themselves believed (and quite rightly!) a loss of NO to have taken place, I cannot conceive how they could expect it to yield accurate results. But apart from this, they seem to ignore that nitrous acid can be perfectly well titrated with potassium permanganate in acid solutions. This process, first proposed by Feldhaus, has been employed for many years by hundreds of chemists, both English and foreign, at all sulphuric acid works, and I showed as early as 1877 that it can be modified so as to combine perfect accuracy with great speed.* Thousands of tests have been made in this way by myself and many other chemists, and it is daily practised in a large number of sulphuric acid works. If Ramsay and Cundall had not employed a solution of caustic soda, but concentrated sulphuric acid, for dissolving their substance, and if they had carried out the titration according to my method, they would have at once obtained the most accurate results which the principle of the process admits of, *i.e.*, not a direct estimation of nitrous acid as such, but that of the quantity of oxygen required for oxidising it up to nitric acid, from which the N_2O_5 can be indirectly calculated. I, for my part, in the numerous researches where I had to estimate nitrous acid along with other nitrogen oxides, have never contented myself with the permanganate method, but I have always combined with it a direct estimation of the nitrogen, thus estimating both N and O. At first I employed Peligot's method with certain modifications, afterwards the method first discovered by Walter Crum, subsequently used by Frankland and Armstrong, and by G. E. Davis, and further developed by myself, on the foundation of testing its accuracy under varying conditions, by the construction of an extremely convenient apparatus, which I have called the Nitrometer.† It is true that Ramsay and

* *Ber.*, 10, 1074. This communication is referred to in my paper (*Ber.*, 11, 1230), quoted by Ramsay and Cundall themselves. My process is also accurately described in my *Treatise on the Manufacture of Sulphuric Acid and Alkali*, in *Lunge and Hurter's Alkali Makers' Pocket Book*, in *Fresenius' Quantitative Analysis*, 2, 569, and elsewhere.

† *Ber.*, 10, 434. The publications of Campbell, Warrington (*Chem. Soc. J.*, 35, 376), and others, subsequent to mine, need not be detailed here. Warrington when carrying out his research, was not acquainted with my nitrometer, although

Cundall ultimately adopted the same principle, but they do not mention the work previously done in this respect, and the apparatus they employ would hardly admit of the thorough and long-continued mixture of the mercury and the acid which it is so easy to attain in the nitrometer,* but difficult to attain with a mercury trough, as experienced by Warington. In point of fact, their analytical results are not very concordant; just the substance with which they make their vapour-density experiments, gave results varying between 31.60 and 32.97 per cent. of nitrogen. Since, moreover, they did not control them by estimating the oxygen, which could have been done so easily and quickly by a proper application of the permanganate method, we cannot in any case consider their analyses as having attained the highest possible degree of accuracy, and this must necessarily influence the validity of the inferences drawn from those analyses with respect of the existence of N_2O_3 in the gaseous state.

We shall now see how far Ramsay and Cundall's observations really support their conclusion that N_2O_3 immediately and completely dissociates on passing into the gaseous state, and hence does not exist at all as a gas. They obtain, by the action of arsenious anhydride on the strongest nitric acid, and cooling, liquids of a greenish or red colour, containing practically nothing but N_2O_4 . By acting on these with a large excess of NO , they ultimately get up to a product containing 31.3 parts of N_2O_3 to 68.7 parts of N_2O_4 , but no further. The passage of oxygen into the blue liquid converts it into $NO_2 + N_2O_4$, but so slowly that they think it is doubtful if the reaction takes place with liquid trioxide. The presence or absence of moisture does not appear to influence the combination.

Evidently all this contributes nothing to the main question, which Ramsay and Cundall seek to decide by estimating the vapour-density of the above-mentioned mixture. They do this by introducing glass bulbs filled with the substance into a tube filled with mercury and inverted in a trough, breaking the bulbs within the tube and measuring the volume of the gas formed within the tube, that is over mercury. From a formula given by J. W. Gibbs, they calculate how far the N_2O_3 present in their substance must have dissociated into molecules of NO_2 , what is the theoretical vapour-density of this mixture, and what the density of the original substance on the

described a year before, otherwise he could have avoided the inaccuracies mentioned by him, p. 386.

* If it were necessary to prove that the nitrometer is very well known and very much employed in England, I might quote the paper by A. H. Allen on new applications of this apparatus, in the *Journal of the Society of Chemical Industry*, 1885, p. 178.

assumption that N_2O_3 had been completely dissociated into NO and $NO_2 + N_2O_4$. With this they compare the densities actually found; and although these do not agree very closely with the theoretical figures, but deviate from them by as many as $2\frac{1}{2}$ units out of about 36, they consider it proved that the N_2O_3 prepared by them does not exist in the state of gas—probably because in most cases the densities found are even lower than those calculated according to their theory.

But do their observations really warrant this conclusion? They work with a liquid containing about 31 per cent. of N_2O_3 without submitting it to the best known analytical methods, so that we cannot be certain of its exact composition, on which everything must depend in this case. They observe the vapour-densities by a process not free from objections, viz., over mercury; they mention themselves that Naumann had found mercury to be slowly attacked by N_2O_4 , and that it was at once somewhat tarnished in their own experiments. This they consider not essential, because they observed no contraction after a few hours' standing; but they overlook that, if NO_2 yields oxygen to mercury, and NO is formed, no change of volume will take place; and if N_2O_4 or N_2O_3 yield $2NO$ under such circumstances, the volume must even be increased, i.e., the vapour-density must be lowered. Thus we do not precisely know what was the real vapour-density of their substance. But even granting, for argument's sake, the correctness of their estimations, the whole method, based upon the change of vapour-densities, is an extremely uncertain one, owing to the presence of nitrogen peroxide. Armstrong, who is altogether disposed in favour of Ramsay and Cundall's view, and even goes beyond them, as we have seen above, still says in discussing the paper, "it was to be hoped that ere long confirmatory evidence that would more directly appeal to chemists would be forthcoming." In other words, even Armstrong implies that those observations, let them be ever so accurate, do not constitute a sufficiently convincing proof of the conclusion based thereon, and other chemists, less favourably pre-disposed for this conclusion, would probably express themselves more strongly in the same sense. Evidently the whole conclusion falls to the ground, if a little more N_2O_4 was dissociated into $2NO_2$ in this case, than Gibbs' formula states for a different condition, viz., for *pure* nitrogen peroxide. But Gibbs' formula cannot lay claim to anything like mathematical accuracy, since the experimental values of the dissociation of N_2O_4 found by the different observers, Playfair and Wanklyn, Sainte-Claire Deville and Troost, Müller, and Naumann, very sensibly differ from one another.

If *everything* were beyond the suspicion of inaccuracy, the analyses of the substance, the method of taking the vapour-densities, Gibbs' formula, its applicability to the case in point, and the coinci-

dence of Ramsay and Cundall's observations with the theory, such extremely indirect argumentation would be convincing; but I consider that I have sufficiently proved that very much indeed is wanting to fulfil these conditions.

The new evidence produced by Ramsay and Cundall in this question is thus seen to be inefficient to solve it. But apart from that, they ought not to have omitted to enter more fully on what had been done before in the same line. Of my labours, pursued through a number of years, and published in a series of communications in the *Berichte* and elsewhere (most of them noticed in the Abstracts of this Journal as well), they say nothing but this: "Lunge has endeavoured to show that the gas absorbed by sulphuric acid consists wholly of N_2O_4 . His argument is that if dissociation were to take place the nitric oxide would escape absorption." Thus they completely pass over that argument which I had pointed out as by far the strongest (to be referred to directly); and what they do quote is perverted into an absurdity, evidently by the above-mentioned neglect of taking into account the concentration of the nitric acid. I, on the contrary, have shown, in opposition to the assertion of others (in several papers which otherwise do not refer to the controversy here treated), that N_2O_4 , which I had proved to be formed from As_2O_3 and strong nitric acid, is completely absorbed by sulphuric acid!

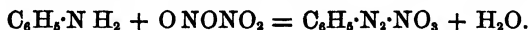
My main argument was as follows:—If N_2O_4 could not exist in the state of gas, but were completely dissociated into a mixture of NO and N_2O_4 (for the sake of simplicity I shall not always add NO_2 , which is evidently unimportant in this case), then, on adding an excess of oxygen to this mixture, all the NO must pass into N_2O_4 , and the analysis must show nothing but N_2O_4 . Opposed to this is the fact (*Ber.*, 11, 1233) that in the gases escaping from vitriol-chambers, which contain a large excess of oxygen, the nitrogen-compounds in normal working conditions show the empirical formula N_2O_3 , whilst the above theory would lead one to expect N_2O_4 . That the empirical composition of the nitrogen oxides in normal chamber-exit gases is really N_2O_3 , and not N_2O_4 , I have since shown in a much more complete and rigorous way in a research carried out with Naef on the vitriol-chamber process (*Chemische Industrie*, 1884, p. 5). The assumption that the compound present in the vitriol-chambers is not N_2O_3 but NO_2H , is excluded by our experiments with chamber gases, since all suspended liquid substances were retained by a long layer of cotton-wool, and hardly anybody will assume NO_2H to exist in the state of vapour. But apart from this indirect argument, I have experimentally investigated the matter in the winter months 1878–1879. The result has been published in abstract (*Ber.*, 12, 357), and in detail (*Dingl. polyt. J.*, 233, 63). I have there proved with cer-

tainty that a gas, evolved from nearly pure liquid N_2O_3 , and carefully analysed, mixed with dry air *never* passes completely into N_2O_4 , even when employing an immense excess of oxygen ($10\frac{1}{2}$ times that required by theory) and working at various temperatures ranging from 4° to 150° . In the presence of 1.7 times as much oxygen as required by theory to convert N_2O_3 into N_2O_4 , as much as 75 per cent. of the N_2O_3 were found to be unchanged, and to have escaped dissociation. As I have minutely described the apparatus and the method of working, and quoted the analytical figures in detail, it would have been easy to criticise or refute any parts of my research that were erroneous. But this has never been attempted from any quarter, and hence my conclusion is not called into question, viz., *that nitrogen trioxide on passing into the state of gas certainly is partly dissociated, but is partly unchanged*. Since, moreover, my experiments plainly show the dissociation of N_2O_3 to increase with an increase in the quantity of air added, and since, on adding such a quantity of air that its oxygen corresponded with 1.7 times that required for oxidising the N_2O_3 to N_2O_4 , still 75 per cent. of N_2O_3 were found to be unchanged, *more than 75 per cent. of N_2O_3 must be left unchanged when simply vapourising without adding any air, and only a comparatively small proportion must be dissociated*. This explains why, on rectifying the blue liquid, no pure N_2O_3 is obtained, a little NO always escaping, but the condensed liquid consists *mostly* of N_2O_3 . The assumption that this N_2O_3 is only formed at the moment of condensation by a combination of NO and N_2O_4 , is rendered very improbable even by Ramsay and Cundall's observation, according to which, *on mixing the vapour of their products with a great excess of nitric oxide and cooling, liquids of at most 31 per cent. N_2O_3 were obtained*. Another observation of those chemists equally supports my results. They found that *liquid nitrogen trioxide is very slowly, if at all, oxidised to N_2O_4 by passing oxygen through it*.* This makes untenable the view held by Armstrong, according to which it was open to assume that Ramsay and Cundall (and, of course, all their predecessors) were dealing with a solution of NO in N_2O_4 . Immediately afterwards, however, Armstrong himself acknowledges this view to be incompatible with the observation that the blue liquid was oxidised with such difficulty, and this must necessarily apply to the gaseous state of N_2O_3 as well, for which I had long ago with all stringency proved a completely analo-

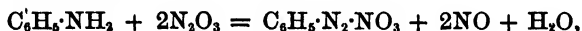
* Hasenbach and Fritzsche say that they converted liquid N_2O_4 , containing N_2O_3 , into pure N_2O_4 by passing oxygen through it and rectifying (Michaelis, *Anorgan. Chemie*, 2, 220). But this is perfectly well explained without the oxygen by the rectifying process alone, since N_2O_4 condenses very easily, but N_2O_3 only at a very low temperature (according to my observations not at all above $-18^\circ C.$), and thus the latter would probably escape, leaving pure N_2O_4 behind.

gous fact. A further argument against the same view is the proof mentioned above, that an excess of NO, brought in contact with liquid or gaseous N_2O_4 , is but slowly and quite incompletely taken up by it to form a substance showing the empirical composition N_2O_3 , whilst it is very easy to prepare the latter directly from As_2O_3 and nitric acid of sp. gr. 1.33.

Hence Armstrong's dictum in the discussion of Ramsay and Cundall's paper: "It was noteworthy that there was no recorded evidence proving the existence of N_2O_3 as gas," is based upon error. Such evidence was produced by me in 1879, and has never been refuted, or even attacked, in any way. That Witt's experiment with aniline (*Ber.*, 12, 1128) does not even touch, and still less refute my main argument, I have proved in *Ber.*, 15, 495; here I shall only say a few words about it. Witt, by passing "Lunge's so-called nitrous anhydride, N_2O_3 ," into a solution of aniline in benzene, obtained diazobenzene nitrate, whilst nitric oxide escaped, and he believed this to prove that the N_2O_3 in the moment of being liberated splits up into N_2O_4 and NO, of which the former alone acts on aniline thus:—



Nitrogen tetroxide he considers, as usual, as the mixed anhydride of nitrous and nitric acid: $NO-O-NO_2$. But there is no difficulty in explaining his reaction by this equation:—



seeing that according to himself (in this respect entirely in concordance with my views) N_2O_4 in contact with sulphuric acid instantaneously yields nitrosyl sulphate and nitric acid, and, on the other hand, NO, acting on a solution of nitric acid in sulphuric acid, immediately furnishes nitrosyl sulphate. All these reactions, as well as the dissociation of N_2O_4 into NO_2 , merely prove how easily the oxygen-atoms combined with nitrogen shift their places; they can no more than mere analyses furnish proof for or against the existence of N_2O_3 in the gaseous state, whilst the facts I have elicited concerning its behaviour towards oxygen can only be explained in the way I have given.

LII.—*On the Reaction between Nitric Oxide and Oxygen under varying Conditions.*

By G. LUNGE.

THE controversy touched upon in the preceding paper has caused me to make some experiments on the behaviour of nitric oxide towards oxygen under different circumstances. I did not think it superfluous to go back to this elementary matter, since some of the statements to be found in the text-books are of very old date, and contain important contradictions. Thus Armstrong in the discussion mentioned in the last paper, quotes Gay-Lussac's experiments of 1816, as proving that $\text{NO} + \text{O}$ always yields nothing but N_2O , the formation of N_2O_3 taking place only in the presence of alkalis. On the other hand, several authors (Dulong, Berzelius, &c.) contend that oxygen with nitric oxide in excess forms N_2O_3 . It is well known that the reaction between NO and O is very materially influenced, not merely by the presence of alkalis, but also by that of sulphuric acid, and even that of pure water; but there are some gaps in our knowledge of these reactions. The experiments to be described below were not made with the intention of thoroughly exhausting this matter, but merely in order to obtain some more evidence concerning the existence of nitrogen trioxide in the gaseous state, and the theory of the vitriol-chamber process.

The apparatus serving for my experiments was so constructed as to avoid any other but glass joints and taps, wherever caoutchouc might be acted on or might cause a diffusion of gases. The oxygen was collected in a graduated cylinder A holding rather more than half a litre, and was delivered from this by means of water pressure, regulated by a screw-clamp. It passed through two drying-bottles charged with concentrated sulphuric acid, and then by means of a glass three-way tap B, at first in the open air, in order to fill all connecting tubes, &c.; afterwards, by changing the position of the tap, it was passed as required into the vessel C filled with nitric oxide. The latter gas was first absorbed in a solution of ferrous sulphate, expelled from this by heat, and collected in an ordinary gas-holder. From here it travelled through two drying-bottles, and was then introduced at the bottom of a Drechsel's washing-bottle C, holding exactly 497.5 c.c., until not merely this bottle, but a further smaller bottle D, and the tube leading away from it, for some time showed no colour whatever, thus proving that all air had been replaced by dry NO . Between C and D a glass tap E was interposed, which was now closed so that the

NO was entirely confined between glass. Now measured quantities of oxygen were forced from A into C through the three-way tap B. Meanwhile the NO had been expelled from D by a current of carbon dioxide, and a certain quantity of pure strong sulphuric acid had been introduced by a dropping funnel. When the reaction in C was finished, the acid contained in D was brought over into C by opening the tap E and constantly keeping up the current of carbon dioxide, which assisted in forcing over the acid and expelled the unabsorbed gas from C through the three-way tap B, turned for this purpose. The sulphuric acid was then tested for the nitrogen oxides dissolved, the nitrogen being estimated by the nitrometer, the oxygen by my modification of the permanganate method, both mentioned in the preceding paper.

I. *Dry Nitric Oxide and Excess of Oxygen.*—Upon 497.5 c.c. NO, which requires just half the volume of oxygen to pass into N_2O_4 , from 400 to 500 c.c. oxygen was allowed to act in three experiments. In one case, the analysis of the sulphuric acid showed that nothing but N_2O_4 had been formed; in the other two cases I found 3.52 and 1.4 per cent. of the nitrogen as N_2O_3 . These quantities—especially the former—exceed the experimental errors possible with my analytical methods, which would support the assumption that even with an excess of oxygen small quantities of N_2O_3 may be formed, but I should not venture to assert this positively on the strength of those few experiments. In any case, dry nitric oxide with an excess of dry oxygen yields almost entirely, perhaps exclusively, N_2O_4 .

II. *Dry Nitric Oxide with an insufficient Quantity of Oxygen.*—To 497.5 c.c. NO only 180 c.c. oxygen was admitted; 124 c.c. O would be required to form N_2O_3 , 249 c.c. O to form N_2O_4 . When the acid began to flow over from D into C, chamber crystals immediately appeared, but of course afterwards dissolved in the excess of acid. On driving out the unabsorbed gas by carbon dioxide no red vapours were noticed in the air. The analysis showed 94 per cent. of the nitrogen to be present as N_2O_3 , 6 per cent. as N_2O_4 . Those who hold that N_2O_3 does not exist as gas, might say that the reaction in C only produced N_2O_4 , NO remaining in excess, and that in contact with sulphuric acid at first the N_2O_4 , as usual, dissolved with formation of nitrosyl sulphate and nitric acid, the latter being then reduced by the NO present to nitrosyl sulphate. But when considering this experiment without any bias, it seems much more simple and nearer the truth to assume that in this case, that is in the presence of an insufficient quantity of oxygen, from the first N_2O_3 was formed (in the state of gas!), along with a little N_2O_4 and some free oxygen, but leaving no NO uncombined. The reasons for this are: 1st, that the chamber crystals *instantly* appeared when the acid came in contact with the

gas; 2nd, both the want of colour of the issuing gas and the analysis of the acid lead to the conclusion that no NO was present, for this does not at all react instantly and completely with nitric acid dissolved in sulphuric acid. This I had found myself in former experiments, and it has been confirmed by others, i.e., by Groves (*Proc. Chem. Sec.*, 1885, p. 24), who remarks that it was difficult to reduce the solution of HNO_3 in H_2SO_4 by NO; 3rd, if primarily no N_2O_3 had been formed, the 180 c.c. O would have combined with 360 c.c. NO to form N_2O_4 , leaving 137.5 c.c. NO in the free state, so that 72.3 per cent. of the nitrogen would have been present as N_2O_4 , 27.7 per cent. as NO. Now, even if these 27.7 per cent. NO had instantly and completely acted in the way mentioned in No. 2, they could not have converted more than an equal percentage of nitrogen present as N_2O_4 into nitrosyl sulphate, thus leaving over 44.6 per cent. nitrogen as N_2O_4 . But analysis showed 94 per cent. nitrogen as N_2O_3 and only 6 per cent. as N_2O_4 . There seems to be no way out of the conclusion, that in the reaction of the gases a considerable quantity of N_2O_3 was formed, along with a little N_2O_4 , leaving some oxygen in excess which, as we have seen in the preceding paper, does not act upon N_2O_3 . This proves that *oxygen with an excess of nitric oxide forms mostly nitrogen trioxide, and furnishes a further proof that nitrogen trioxide exists in the state of gas.*

III. *Nitric Oxide and Excess of Oxygen in the presence of Moisture.*—The vessel C, before filling it with oxygen, was rinsed with water, so that a very few drops remained therein; 497.5 c.c. NO and 375 c.c. oxygen were employed. When these were mixed, a strong vacuum was formed in C, the acid rushing into it with vehemence when the tap E was opened, and absorbing the gas. Analysis showed 98 per cent. of the nitrogen to have passed over into nitric acid, and 2 per cent. into N_2O_4 . Hence that minimal quantity of water had sufficed for giving a totally different character to the action; NO now passed almost entirely, and with more water no doubt would have passed altogether into HNO_3 . Whether an intermediary formation of HNO_2 took place or not, the experiment did not show; certainly no green colour of the drops could be observed.

IV. *Nitric Oxide and Excess of Oxygen in the presence of Dilute Sulphuric Acid.*—The acid was taken at sp. gr. 1.405, because acids of something like that concentration, according to my former researches, can contain only traces of nitrosyl sulphate, whence it might be inferred that they would not act in favour of the formation of that compound; it remained to be seen whether for all that the presence of sulphuric acid would induce the formation of N_2O_3 . The vessel C was charged with 10 c.c. sulphuric acid of sp. gr. 1.405, and with the remaining 487.5 c.c. NO there was mixed 365 c.c. oxygen, which had

to bubble through the acid. The atmosphere of the vessel as usual assumed a reddish-brown colour, the acid gradually a slight green colour. After standing a quarter of an hour 50 c.c. of strong sulphuric acid was introduced, which at once absorbed the reddish gas—carbon dioxide being passed through as before. The analysis of the acid showed that 89·8 per cent. of the nitrogen was present as nitric acid, and 10·2 per cent. as nitrosyl sulphate. Hence we must conclude that the dilute sulphuric acid acted on the whole like water, that is, it induced the oxidation of NO up to HNO_3 . Still it is seen that, even at that dilution, sulphuric acid to a certain extent favours the formation of N_2O_3 , probably so far as nitrous acid forms a stable solution in the acid, which seems to produce the green colour. Owing to the complication of the conditions I would not draw any definite conclusions from this experiment.

V. *Nitric Oxide and Oxygen in Excess, in the presence of Concentrated Sulphuric Acid.*—An experiment in this direction was performed against my will the first time I operated, when the glass tap E had not yet been provided, as during the passage of oxygen into the vessel C holding the NO, the sulphuric acid from D passed back into C. Thus the combination between O and NO took place at first in the absence, subsequently in the presence of strong sulphuric acid. The result was that 39·4 per cent. of the nitrogen was found as N_2O_3 , and 60·6 per cent. as N_2O_4 .

A further experiment was then made in this way. The vessel C was first charged with 50 c.c. strong sulphuric acid and then filled with oxygen, several litres of this gas being passed through the acid and away through E and D. There would now be 447·5 c.c. O in the vessel C. The nitric oxide was this time put into A, and 370 c.c. of this was very gradually forced over into C, so that at first only one or at most two bubbles per second passed through the acid, which was shaken up from time to time. Thus each bubble of NO met with an enormous excess of oxygen, but mostly in immediate contact with concentrated sulphuric acid. The colour of the gas was very faintly yellow; later on, when, in consequence of the partial vacuum in C, the NO passed over more rapidly, the colour deepened to some extent. On the sides of the cylinder, wetted with acid on shaking about, a strong formation of chamber-crystals took place. After all the NO had been introduced, the whole was allowed to stand a quarter of an hour, the yellow colour gradually disappearing. The final analysis showed 68·7 per cent. of nitrogen to have passed into N_2O_3 , 31·3 per cent. into N_2O_4 . Since, of course, as shown by the yellow colour, part of the NO did not combine with oxygen in immediate contact with the acid, but higher up in the cylinder, we arrive at the following conclusion. Where nitric oxide meets with

oxygen, even with an enormous excess of this, but in immediate contact with concentrated sulphuric acid, N_2O_3 is formed, which at once combines with sulphuric acid to form nitrosyl sulphate; but further on, that is, in the space above the acid, the ordinary reaction $2NO + O_2 = N_2O_4$ takes place. This completely agrees with previous observations. On the one hand, it has been observed, first by C. Winkler, and confirmed by myself in several series of experiments, part of which have been published, that, when strong sulphuric acid, oxygen, and nitric oxide meet at the same time, *e.g.*, if nitric oxide and oxygen are made to bubble up through the acid side by side, the acid is found to contain nothing but N_2O_3 , *i.e.*, nitrosyl sulphate. On the other hand, I had formerly found that, when the two gases are passed through the acid so quickly that they are not entirely absorbed and can only combine completely in the upper part of the vessel, and when the product here formed is absorbed in a second bottle charged with sulphuric acid, analysis of the latter shows it to be composed of N_2O_4 . Hence there is nothing like a "catalytic" action of sulphuric acid for determining the combination of $2N$ with $3O$, without any share in this being taken by H_2SO_4 ; the sulphuric acid only acts if it can itself enter into the combination.

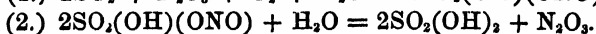
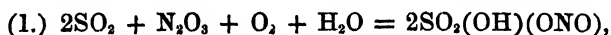
The conclusions to be drawn from the above-described experiments can be formulated thus:—

1. In the dry state, nitric oxide with an excess of oxygen combines to form N_2O_3 exclusively, or nearly so.
2. Dry nitric oxide and oxygen with an excess of the former, yield a great deal of N_2O_3 along with N_2O_4 , both in the state of gas.
3. In the presence of water, nitric oxide, with an excess of oxygen, is altogether converted into HNO_3 .
4. If nitric oxide and oxygen meet in the presence of concentrated sulphuric acid, there is neither N_2O_4 nor HNO_3 formed, even with the greatest excess of oxygen, but the reaction is—



Regarding the theory of the vitriol-chamber process, the above-established facts, taken in connection with those elicited by myself and Naef from the examination of a working set of chambers (*Chemische Industrie*, 1884, p. 5), where it was proved that under normal conditions the back chambers contain no N_2O_4 , but N_2O_3 , lead to the following conclusions. Since the chamber always contains an enormous excess of oxygen, any NO (which according to the general assumption as held hitherto is being constantly liberated) must principally pass into N_2O_4 ; for the particles of sulphuric acid, floating about in the shape of a mist, cannot act on the molecules of gas coming in contact with one another at some distance from the acid.

particles. But it has been established that little or no N_2O_4 is formed so long as there is any appreciable formation of H_2SO_4 , i.e., so long as appreciable quantities of SO_2 are present in the chamber. Hence no free NO can be given off at all, but the process must take place in the following phases, both of them very well-known reactions:—



That is, sulphur dioxide combines directly with nitrogen trioxide, oxygen, and a little water to form nitrosyl sulphate, which floats in the chamber as a mist; on meeting an excess of water, equally floating about as a mist, the nitrosyl sulphate splits up into sulphuric acid, which sinks to the bottom, and nitrogen trioxide, which begins to act anew. *Hence it is not, as hitherto generally assumed, the nitric oxide, NO, but the nitrogen trioxide, N_2O_3 , which acts as carrier of the oxygen in the vitriol-chamber process.* This process is to some extent modified in the first part of the set of chambers by the excess of SO_2 , in the last part sometimes by the complete absence of SO_2 , and in some places by an excess of water. On this, as well as on several other points of importance, I shall enter in a special communication to be published later on.

[ADDENDUM.—After the above two papers had been read, Dr. Armstrong made some observations to which I beg to reply here, as I was not present at the meeting. Dr. Armstrong says that my results are vitiated by the fact that NO reduces NO_3H to the nitrous state. This is a mistake; in the only case where that reaction comes into play (Experiment No. II), I have shown that, even if the reducing action of NO is assumed to have taken place to the fullest possible extent, a large excess of N_2O_3 remains unaccounted for by any other theory than that it existed in the gaseous state. With my experiments of 1879 that action of NO has no connection whatever. Dr. Armstrong says it is probable that in those experiments the gases never became thoroughly mixed. This is also a mistake; the gases (that is, the vapour of N_2O_3 and a large excess of atmospheric air) were introduced in concentric layers at the top of a U-tube, kept at different temperatures, from 4—150° (where the changes of temperature must have produced constant currents), were passed along the tube and through some very narrow tubing into sulphuric acid, where all the absorbable part was taken up. It is hardly conceivable that in this way any NO could have escaped coming into contact with oxygen present up to 10½ times the theoretical quantity, and practically impossible that this should have taken place to the extent observed, namely, up to 75 per cent. of the total nitrogen compounds present. Lastly, Dr. Armstrong

says that Naef's and my own observations on the composition of the chamber gases are a complete riddle to him. Those observations, extending over several months, are *facts*, and must be dealt with as such; they cease to be a riddle the moment one drops the idea that N_2O_3 cannot exist as a gas. That N_2O_3 once formed is not oxidised by any excess of O has been proved by myself for the gaseous state, and by Ramsay and Cundall for the liquid state. If there are really no other objections to my views than those advanced by Dr. Armstrong, then it must be considered as definitely proved that N_2O_3 exists as a gas.]

LIII.—*Detection and Estimation of Iodine.*

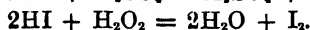
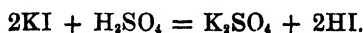
By ERNEST H. COOK, B.Sc. (Lond.), A.R.C.S., Bristol Trade and Mining School.

ALTHOUGH the liberation of iodine from the iodides and its recognition when liberated by means of starch is a matter of great ease and delicacy, yet the detection of small quantities of iodides when mixed with relatively large quantities of bromides and of small quantities of bromides when mixed with iodides, is a matter of some difficulty. This difficulty is very much increased when we endeavour to estimate the amounts of the various salts in a mixture. If we inquire as to the cause of this, we find that it is due, firstly, to the circumstance that most substances which liberate iodine from its compounds also liberate bromine; and secondly, that we have no solvent for iodine which will not at the same time dissolve bromine. We are thus bound to adopt either a different method altogether (as, for example, the reactions of hydriodic acid with palladious salts, and the formation of cuprous iodide) or to effect a partial separation by the cautious use of nitrous acid, chlorine, or some substance which will liberate the halogens from their combinations. The first of these alternative methods is seldom employed, and the detection and estimation of iodides is almost invariably effected by the use of either nitrous acid or chlorine. The difficulties attending the use of these reagents are that if an excess of nitrous acid be used, bromine will be liberated as well as the iodine, whilst if an excess of chlorine be employed not only will this occur, but colourless chlorides of iodine and bromine also be formed. If we could employ some substance which would liberate the iodine and not the bromine these difficulties would be much reduced and the process simplified. The object of this paper is to propose the use of such a reagent.

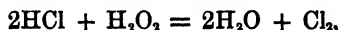
If hydrogen peroxide is added to potassic iodide an immediate separation of iodine occurs, and an abundant evolution of oxygen takes place. When added to potassic bromide or chloride, oxygen is also given off, but no bromine or chlorine is set free. These facts were noted by Schöne (*Annalen*, 195, 228—252), who also states that it is impossible thus to separate the whole of the iodine of the potassium iodide. This latter statement I have confirmed, for after standing for several days the application of chlorine water, after boiling off the undecomposed hydrogen peroxide, would invariably produce a further separation of iodine. I find, however, that if an excess of acid is present no oxygen is evolved, but the whole of the iodine is separated in the free state. The reactions which will take place being the following:—



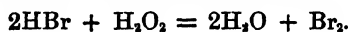
Under similar circumstances neither bromine or chlorine are separated from their compounds. This is the test which I venture to propose, as it affords not only a means of detecting small quantities of iodine in presence of large quantities of bromine, but also lends itself to quantitative determinations. When acids stronger than acetic acid, or those which produce a change of state (for example, tartaric, which precipitates potassium) in the solutions, are used, then the first action is probably the formation of hydriodic acid, which is afterwards split up by the peroxide, depositing the whole of its iodine, thus:—



In the case of hydrochloric acid, this liberation is brought about by the action of the nascent chlorine evolved by the action of the hydrogen peroxide on the acid, thus:—



A similar action occurs with hydrobromic acid:—



It is therefore evident that any acid which is capable of decomposing the bromide is quite unsuitable for the proposed test, as the result of the action would be the liberation of bromine along with the iodine. The action with comparatively weak acids (such as acetic) is interesting, as it illustrates the effect of removing from the sphere of action one of the substances produced by that action. Thus, as has been stated above, hydrogen peroxide will only partially decompose potassic

iodide, producing potassic hydroxide. If, however, an excess of acid be present to combine with the alkali thus produced, then the whole of the iodide will be decomposed. On the other hand, this result is not due to the preliminary decomposition of the iodide by the acid, for if acetic acid is added to potassic iodide, and the mixture exposed to light, no separation of iodine occurs, as would be the case if hydriodic acid had been formed. The mode of employing the reagent is as follows, the hydriodic acid being present as alkaline salt.

For Qualitative Purposes.—Acidify with acetic acid and add one or two cubic centimetres of peroxide (the commercial solution answers all requirements). If an iodide is present an immediate separation of iodine occurs.

For Quantitative Determinations.—The solution is made strongly acid with acetic acid, and sufficient hydrogen peroxide added to liberate the iodine. (For quantities of potassium iodide up to 1 gram 5 c.c. of hydrogen peroxide will be found ample.) The mixture is now allowed to stand from 30 to 60 minutes, when the whole of the iodine will be separated, some being deposited in the solid state. The liberated iodine is dissolved in chloroform, and the solution thus formed carefully syphoned off, washed with a little water, and titrated with standard thiosulphate solution. The process will be found to give very accurate results after the little manipulative skill necessary has been acquired. I have advised dissolving in chloroform because it is colourless, and there is no residual tint to mask the point of final disappearance of the iodine colour. Starch solution may be added towards the end of the titration, but I have obtained equally good results without its use as with it. There is one important precaution which it is necessary to observe, and that is to wash the chloroform solution quite free from any peroxide. The reason of this is that on the addition of the thiosulphate solution to the iodine, sodium iodide is produced, which will be immediately decomposed by the hydrogen peroxide with the separation of iodine. Thus, after producing a colourless liquid by running in the sodic thiosulphate, if the mixture is allowed to stand, a separation of iodine will occur if the washing has been imperfectly performed.

The following results will illustrate the accuracy of the method. They were obtained without making use of extra precautions to ensure exactness, and no doubt a little more care would give closer approximations.

Estimation of Iodine.

Experi- ment.	Amount of iodine taken.	Amount of bromine taken.	Amount of chlorine taken.	Amount of iodine found.	Percentage found.
1	0·0259	0·2645	—	0·0256	98·8
2	0·0518	0·1322	—	0·0513	99·0
3	0·1295	0·2645	0·1163	0·1285	99·2
4	0·0518	—	0·1163	0·0518	100·0
5	0·0518	0·2645	—	0·0515	99·4
6	0·0518	0·1322	0·0582	0·0513	99·0
7	0·1036	0·5290	—	0·1027	99·1
8	0·1036	0·2645	0·1163	0·1025	98·9
9	0·0777	0·5290	0·2326	0·0791	101·8*
10	0·1295	0·1322	0·2326	0·1288	99·5

LIV.—The Selective Alteration of the Constituents of Cast Iron.

By THOMAS TURNER, Assoc. R.S.M., Demonstrator of Chemistry,
Mason College.

IN a former paper (*Trans.*, 1884, 260) reference was made to experiments now nearly completed, which were undertaken with a view of ascertaining the influence of silicon on the properties of iron and steel. The original plan of experiment was very simple, although it became necessary to introduce modifications as the work progressed. It was intended to mix iron, in a state of commercial purity, with different proportions of silicon-pig, containing if possible only iron, silicon, and carbon; then, by preparing test pieces from the several products, to ascertain the influence of silicon on the mechanical properties of the metal.

But, on making inquiries for a commercial article which would correspond to the ideal silicon-pig required, considerable difficulty was experienced in obtaining a suitable material. But at length, through the Patent Shaft and Axle Company, of Wednesbury, a metal was obtained which appeared to be more suitable for the purpose than any other which had been met with. Its composition was as follows:—

Total carbon	1·81 per cent.
Graphite	1·12 ,,
Manganese	1·95 ,,
Sulphur	0·04 ,,
Phosphorus	0·21 ,,
Silicon	9·80 ,,

* In this case the washing was imperfectly performed.

Hence, although this pig possessed many characters which recommended its adoption, there was the disadvantage that the amount of manganese was by no means inconsiderable, amounting to one-fifth of the silicon present. The following experiments were undertaken with a view of diminishing the amount of manganese, but of leaving the silicon, if possible, unaltered.

It is well known that when a mixture of iron and manganese is exposed to the action of oxidising agents, either with or without the simultaneous presence of other elements, the manganese becomes first oxidised, and, in presence of silicon, is removed as slag. This fact is applied in the puddling furnace, and in the production of Bessemer steel. It is further noticed by the manufacturer, on adding ferromanganese to a bath of molten steel, that the amount of manganese which remains in the metal is less than that which has been added, and this difference has been accounted for by assuming that ferrous silicate possesses the property of removing manganese from iron when in the fused condition. The following experiments were commenced on that supposition; the intention being, if possible, to eliminate the manganese, without materially altering the amount of silicon present.

In each case, the quantity of silicon-pig operated on was 2 kilos., which was placed in small lumps in a crucible of Stourbridge fireclay, and covered with a plumbago lid; the whole being placed on a brick in a coke furnace, and the fire built round it. In about an hour the metal becomes perfectly fluid and is thoroughly stirred; it is then kept in contact with the materials added, for from one to two hours, the lid being removed at intervals, and the contents of the crucible thoroughly stirred by means of an iron rod. The crucible is then removed, allowed to cool, broken, and the contents examined.

The substances employed for the removal of the manganese were of two kinds, acid and basic. The acid material was silica, and the basic substance was oxide of iron.

I. To produce a perfectly *fluid acid slag*, 200 grams of powdered glass and 50 grams of fine white sand were mixed with 30 grams of sodium bicarbonate, and the whole kept fluid and well stirred at intervals for two hours. The product contained—

Silicon .. = 9.45

Manganese = 1.89

or the silicon ratio, $\frac{\text{silicon}}{\text{manganese}} = 5$, whilst in the original material the ratio was 5.02. Hence, there was no change in the relative proportions of the two elements present, and the character of the iron was unaltered.

II. To obtain a more acid mixture, 50 grams of glass were mixed with 50 grams of sand, both in fine powder, and the whole heated for $1\frac{1}{2}$ hours with frequent stirring. The slag was less fluid than before, although on cooling it was still quite glassy, and of a deep olive colour. The loss of metal in the previous experiment was 1 per cent., in this case it was greater—being 2.1 per cent. The product contained—

Total carbon.....	1.72
Manganese	1.78
Silicon	9.46

The "silicon ratio" was therefore 5.31, a slight increase, but the character of the metal was unaltered.

III. In this experiment, sand alone was employed, 50 grams being used to 2 kilos. of iron. The metal was kept fused one hour, being frequently thoroughly stirred. The sand gradually became pasty, and on cooling was black, having evidently been partly converted into silicate. But the material was not at any time fluid, and on analysis the composition was found to be—

Total carbon	1.67
Manganese	1.85
Silicon	9.73

The silicon ratio being 5.26, not a very marked alteration. Probably the only effect of the sand in these cases was to help to keep the silicon constant, the active agent being oxidation during melting and stirring.

IV. To obtain a *fluid basic* slag, 120 grams of ferric oxide, and 50 grams of sand, were mixed with 15 grams of powdered coke. These proportions were employed to produce a ferrous silicate containing upwards of 50 per cent. of iron, and corresponding to tap cinder of the puddling furnace. The whole was strongly heated, as before, with 2 kilos. of silicon-pig, and well stirred at intervals during $1\frac{1}{2}$ hours. The slag produced was tolerably fluid. But on analysis, the following results were obtained:—

Silicon ..	= 9.50
Manganese	= 1.91

or the silicon ratio = 5 nearly. Hence the action of the slag was practically *nil*, as the slight change in composition which was observed might have been readily produced during the melting of the metal.

V. In this experiment ferric oxide mixed with sand was used. 30 grams of sand were placed on the bottom of the pot, the usual quantity of silicon-pig introduced, and then a mixture of 120 grams of ferric oxide with 45 grams of sand. The metal was kept fused for $1\frac{1}{2}$ hours

and frequently stirred. A pasty slag was produced, and 7·4 per cent. of the metal employed was lost. On analysis it gave—

Carbon .. = 1·69

Manganese = 1·58

Silicon .. = 9·54

or silicon ratio = 6·04, a marked increase.

VI. In this case, ferric oxide alone was employed; 200 grams were made into a paste with water, and the crucible lined with the paste. It was then dried, and 2 kilos. of silicon-pig fused in it for two hours with frequent stirring. The loss was not great, being 2·5 per cent., and the character of the pig appeared unaltered. On analysis it gave—

Silicon .. = 8·27

Manganese = 1·25

or silicon ratio = 6·62, being a further marked increase—although it will be noticed at the same time that the silicon is considerably diminished.

VII. To render the comparison more complete, 2 kilos. of silicon-pig were melted, and air was blown through the metal for five minutes by means of a single clay tube. The product was then analysed, and yielded—

Silicon .. = 8·87

Manganese = 1·12

or silicon ratio = 7·92, a still greater increase.

We may now arrange the silicon ratios from the different experiments as follows:—

Material used.	Ratio $\frac{Si}{Mn}$.
Original silicon-pig.....	5·02
Ferrous silicate	4·98
Fluid acid slag.....	5·00
Sand.....	5·26
Sand and glass.....	5·31
Sand and ferric oxide	6·04
Ferric oxide.....	6·62
Air blown.....	7·92

From these results we may conclude—

1. That ferrous silicate, apart from atmospheric oxygen, is not capable of oxidising manganese in pig-iron.

2. That ferric oxide alone, or atmospheric air alone, readily oxidises manganese in pig-iron, but that the manganese is only oxidised simultaneously with other elements.

From the fact that manganese is more readily oxidisable than iron, it might have appeared that ferrous silicate would itself probably act as an oxidising agent in the removal of manganese from iron. But these experiments appear to show that the real action of ferrous silicate is rather that of a carrier of oxygen than of a true oxidising agent. Ferric oxide is first formed, and this is reduced by the bath of metal present.

Further, these experiments tend to confirm the practice of the present day, as showing that when it is desired to selectively alter the constituents of iron or steel it must be effected, not by attempting to eliminate some obnoxious material, which can only be accomplished by seriously altering the amounts of other elements present, but it must be done by starting from a pure metal and adding the constituent or constituents which are desired.

In conclusion I would gratefully acknowledge the important help I have received from Mr. J. P. Walton, Assoc. R.S.M., of the Wishaw Iron Works, who has performed one half of the analyses recorded in this paper.

LV.—On some Sulphur Compounds of Calcium.

By V. H. VELEY, M.A., F.I.C., of the Laboratory, Christ Church,
Oxford.

V. To obt:

Oxon

Introductory.

THOUGH the sulphides of calcium form an integral part of two important industries, viz., the Leblanc soda process and the purification of coal-gas, yet up to the last few months these substances have received but little attention at the hands of investigators.

It appeared worthy of interest, with a view to a particular study of the chemical changes involved in the latter industry, to determine the composition of the substances formed (1) by the action of hydrogen sulphide on calcium hydroxide, and (2) of carbon disulphide on the resultant material.

Historical.

Calcium Sulphide.—Berzelius, in his monograph on the sulphides of the alkali metals (*Schweigger's Journal*, 34, 12), describes a process for the preparation of calcium sulphide by passing hydrogen sulphide over red-hot lime (free from water and carbonic anhydride). The

equivalent weights of the water and calcium sulphide formed in accordance with the equation—



were found to be in the proportion of 87 : 89, or practically 1 : 1.

In another memoir Berzelius (*Pogg. Ann.*, **6**, 442) obtained by the evaporation of the liquid formed by the continued action of hydrogen sulphide on calcium hydroxide, crystalline needles of hydrated calcium sulphide, to which, in accordance with more modern views, the name calcium hydroxyhydrosulphide is assigned.

On the other hand, Rose (*Pogg. Ann.*, **55**, 443) states that calcium sulphide, when boiled with water, yields the hydrosulphide which dissolves, and the hydroxide which remains undissolved. From the solution on evaporation acicular crystals separate out, to which Rose ascribes a composition $\text{Ca}_6\text{S}_6\text{O}_6, 20\text{H}_2\text{O}$, presumably calcium hydroxyhydrosulphide, with a slight excess of calcium oxide, and formed according to the equation—



While this work was in progress, there appeared a most important and interesting communication by Divers and Schmidzu (*Trans*, 1884 278), on the preparation and properties of crystalline calcium hydrosulphide and hydroxyhydrosulphide, and of the amorphous sulphide; this has thrown considerable light on the constitution of these compounds, and materially assisted the author in the later part of his investigations.

Short notices of oxygenated sulphur compounds of calcium have also been published by Folkard (*Chem. News*, **49**, 258; *Abstr.*, 1884, 892) and W. Foster (*Journal of Gas Lighting*, September 30, 1884).

Calcium Sulphocarbonate or Thiocarbonate.—In another memoir (*Pogg. Ann.*, **6**, 444), Berzelius describes the preparation of this salt by digesting together calcium sulphide, water, and carbon disulphide, at a temperature of 30°, air being excluded throughout the experiment. The sulphide is gradually dissolved, with production of a deep red liquid, from which, on evaporation in a vacuum, there separated a red confusedly crystalline red mass. With hydrochloric acid, the solution of the salt gave a red oil, described also by Zeise, probably thiocarbonic acid. A solution of calcium thiocarbonate gives with solution of salts of the heavy metals, dark brown precipitates, with nickel and manganese salts, olive-green solutions, with ferrous salts a deep wine-red coloration, and with zinc-salts a golden white precipitate. These various substances emit carbon disulphide when heated, leaving a residue of the sulphide, oxide, or carbonate, according to the nature of the metal. Calcium thiocarbonate on exposure

to the air is slowly converted into the carbonate, a change immediately effected by heating to 60—80°; in concentrated solutions it gives off carbon disulphide, leaving a residue of calcium sulphide.

D. Walker (*Chem. News*, 30, 28) describes a calcium thiocarbonate, $\text{CaCS}_3 \cdot 2\text{Ca}(\text{OH})_2 + 6\text{H}_2\text{O}$, prepared by agitating milk of lime with carbon disulphide; it is described as crystallising in light orange-yellow needles, soluble to a small extent in cold water, yielding an orange-yellow solution, from which, on addition of hydrochloric acid, yellow oily drops of thiocarbonic acid separate out. These several investigations will be alluded to in the course of the present paper.

Preparation of Calcium Sulphide in the Dry Way.

The method of preparing calcium sulphide described by Berzelius, which consists in passing hydrogen sulphide over calcium oxide or hydroxide, was adopted in outline, and it was thought that a better insight might be gained into the nature of the change if the weights of calcium hydroxide used, and of calcium sulphide and water formed, could be determined accurately.

In the first experiment, selected transparent crystals of Iceland spar were used for the preparation of the calcium oxide, but further investigations showed that even the best specimens contained traces of ferric oxide, alumina, and silica. To eliminate these impurities, the crystals were dissolved in dilute hydrochloric acid, and the solution evaporated to dryness to separate out silica; the chloride was then redissolved, a few drops of nitric acid added, and the iron precipitated as ferric oxide, together with the alumina. The filtrate from this was fractionally precipitated by ammonium carbonate, the first portions containing invariably traces of iron (derived possibly from the carbonate), together probably with small quantities of barium and strontium. The carbonate was then washed free from chloride by decantation. In order to convert the carbonate into oxide, it was heated either in a porcelain tube, in a current of hydrogen or steam, those portions of the material at the two ends of the tube being invariably rejected; or the carbonate was placed within a platinum crucible, enclosed within a fireclay crucible, the space between them being packed with crude lime, and the whole heated in a gas furnace. The presence of lime prevents the reabsorption of carbonic anhydride on cooling, and also the formation of hard non-friable masses, which were occasionally produced when the products of the combustion of the coal-gas came into direct contact with the carbonate. The product contained only the smallest traces of carbonate, and dissolved perfectly when it was suspended in water and hydrogen sulphide passed in. In the course of the work, most marked evidence was obtained as to

the delicate nature of this test for the purity of calcium oxide, as suggested by Divers. In fact it was this test alone which caused the substitution of calcium oxide prepared by the process described above for that prepared from Iceland spar. The resultant oxide contained only the smallest traces of carbonate.

Hydration of the Oxide.—The hydration of the oxide, under conditions precluding contact with carbonic anhydride, was effected as follows:—A watch-glass containing a weighed sample of the oxide was placed at the top of a glass cylinder, with both ends open; over this was inverted another cylinder of rather larger diameter, and the two placed in a beaker containing a hot solution of sodium hydroxide. The apparatus was kept for some time in a warm place, until the oxide was converted into the hydroxide, the excess of water being removed by drying over calcium chloride.

In order to show the accuracy of this process, the following results may be cited:—

Weight of CaO taken.	Weight of Ca(OH) ₂ formed.	Ratio of $\frac{\text{Ca(OH)}_2}{\text{CaO}}$.	
		Found.	Theory.
3.5734	4.7314	1.3242	1.3216
3.5776	4.7324	1.3215	—
3.8574	5.0679	1.3136	—
3.9473	5.190	1.3145	—
Mean....		1.3144	1.3216

The calcium hydroxide was then transferred as quickly as possible into a cylindrical tube, tapering gradually at the lower end, then bent at a right angle; on the limb is blown a bulb, beyond which it is bent through an angle of 180°, and drawn off at its lower extremity into a fine point. This apparatus was found to be the most suitable for the elimination of the water, which was apt to form damp masses of the sulphide, and thus choke up the tube.

A ground glass stopper fitted with a limb bent at right angles with a stopcock closed the upper end, and the lower or tapering end was partially closed with a loosely fitting glass bulb, to prevent the hydrate from falling into the limb of the tube. This apparatus will for brevity sake be designated "the lime tube." The upper limb of this tube was connected with a T-piece, through one arm of which could be passed hydrogen, and through the other hydrogen sulphide, each arm being fitted with a stopcock. The hydrogen was purified and dried by passing it through potassium chromate solution, strong sulphuric acid, sticks of solid potash, and calcium chloride, whilst the hydrogen sulphide (from iron pyrites and hydrochloric acid) was purified by

washing with water, passing it through damp iron sulphide to stop traces of oxygen, and finally dried. The water formed in the reaction was collected in a U-tube filled with calcium chloride, the form being that used in combustion analysis, with one limb bent up, into which passed the drawn-out extremity of the lime tube. As a necessary precaution, the calcium chloride in the hydrogen and hydrogen sulphide apparatus, and in the collecting tube, was always taken simultaneously from the same sample. During the passage of the hydrogen sulphide, the lime tube was heated to a temperature of 60° , in a square copper box filled with water; through a cork at the bottom of this passed the drawn-out extremity of the lime tube. The temperature of the water was maintained constant by means of the automatic mercury and oil gas regulator, described at length in a former paper* (Trans., 1883, 371); water was also supplied from a water level regulator.

Method of Analysis used.—Sulphur was determined by Carius' method for the determination of sulphur in organic substances.

Calcium was estimated by oxidation by nitric acid in the above process, and precipitating the calcium sulphate by ammonium oxalate, or (2) by evaporating the substance with dilute sulphuric acid to which was added a little nitric acid, and weighing the sulphate formed; water and carbon, if present, by the usual processes of organic analysis.

Preliminary experiments showed that at first, on passage of the hydrogen sulphide, the calcium hydroxide gained considerably in weight, and but small quantities of water were eliminated; but on continuing the process the weight of the product was approximately equal to the original hydroxide. This result would accord with the conversion of the hydroxide, $\text{Ca}(\text{OH})_2$, into the sulphide CaS , the molecular weights of which are in the ratio of 74 : 72.

Series I.

Constant temperature 60° . In this series the water evolved was not estimated.

Conditions of experiment.	Time.	Weight of contents of lime tube.	Difference.
— .. —	—	5.0596	—
Hydrogen sulphide passed..	3 days	5.0242	— 0.0304 gr.
„ „ „ ..	12 hours	5.0242	nil.

* In order to show the degree of constancy obtainable by the regulator, I may mention that an instrument supplied to Professor Moseley's Anatomical Department for an incubating apparatus has maintained the temperature constant within one degree for two years.

Analysis of Resultant Material.

	Found.	Mean.
Calcium as CaSO_4 ..	53.44, 53.42 per cent.	53.43
Sulphur as BaSO_4	43.13 "	43.13
Water	3.2 "	3.20
		<hr/> 99.76

Atomic proportion of calcium to sulphur 1 : 1.009.

The substance is thus calcium monosulphide, CaS , containing a small proportion of water. On comparing the analytical and synthetical numbers, supposing that 3.2 per cent. of the water is retained by the resultant sulphide, then the following results obtain:—

	Theory.	Experiment.
Calcium hydroxide	5.0246	5.0246
Calcium sulphide	4.8793	4.8638

The error is less than 1 per cent, the small difference arising doubtless either from slight oxidation of the sulphide, or from a small quantity of the hydroxide escaping transformation into the sulphide.

The experiments were repeated at the same temperature of 60° ; owing to a temporary block, the temperature was raised for a short time to drive forward the water.

Series II.

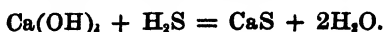
Conditions of experiment.	Temp.	Time.	Weight of contents of lime tube.	Diff.	H_2O collected.
—	—	—	4.240	—	—
Hydrogen sulphide passed	60°	36 hours	4.250	+ 0.01	1.9477
"	90	1 hour			
"	70	14 hours			
"	60	20 "	4.215	— 0.045	0.035
Net results			—	— 0.035	+ 1.0827

Analysis of Resultant Material.

	Found.
Calcium as CaSO_4	54.21 per cent.
Sulphur as BaSO_4	43.57 "
Water.....	1.97 "
	<hr/> 99.75 "

Atomic proportion of calcium to sulphur 1 : 1.004.

The reaction is thus practically represented by the equation—



If the 2 per cent. found by analysis of the sulphide be transferred to the water collected in the tube, then the synthetical and analytical results will compare as follows:—

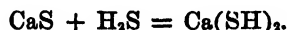
	Theory.	Experiment.
Calcium hydroxide..	4.24	4.24
Calcium sulphide } obtained }	4.121	4.125 { reckoned in the anhydrous state.
Water formed	2.071	2.053

These numbers are within the limits of experimental error.

Conditions of Formation in the Dry Way.

In the course of this investigation it was observed that perfectly dry calcium oxide was unaltered by perfectly dry hydrogen sulphide; this result is analogous to the well-known fact, often demonstrated as a lecture experiment, that dry calcium oxide does not absorb dry carbonic anhydride. But the former case is the more remarkable, in that it would appear more *a priori* probable that the elimination of an infinitesimally small quantity of water would cause the reaction to proceed to its final completion. Another example is thus afforded of the necessity of the intervention of a third substance to bring about the reaction of two others.

It was noticed that the excess of hydrogen sulphide was retained with considerable pertinacity, probably owing to the solution of calcium oxide in the water, and formation of calcium hydrosulphide, or the direct combination of the calcium sulphide with hydrogen sulphide, thus:



Properties of Calcium Sulphide.

Anhydrous calcium sulphide when freshly prepared is a white powder, emitting a considerable odour of hydrogen sulphide when exposed to the air; if moistened, it turns of a pale yellow tint, probably due to the formation of oxidised products (cf. Divers, *supra*). The various samples of calcium sulphide prepared by Divers and the author were quite colourless, but there appears to be some misapprehension regarding the colour of these substances, for they are described in various text-books as possessing a blue tint, and even recently in the *Journal of Gas Lighting*, September 30th, 1884,

A. Foster mentions a greyish-blue calcium oxysulphide. Some small quantity of a bright blue material, obtained in the course of the dissolution of calcium oxide prepared from Iceland spar, was examined qualitatively. It was washed at first several times with cold water, and then repeatedly with hot water; the residue dissolved in hydrochloric acid with evolution of hydrogen sulphide. The solution contained aluminium, silica, and calcium in some quantity, and traces of iron, derived from impurities contained in the calcium oxide.

Preparation of Calcium Hydrosulphide in the Wet Way

has been made the subject of an extensive research by Divers, whose experiments would not have been repeated, had it not appeared that the process might offer a convenient method for the preparation of the thiocarbonate, and to decide whether the calcium oxide is completely converted into calcium hydrosulphide by the hydrogen sulphide, supposing the resultant solution to be sufficiently dilute. An apparatus similar to that described by Divers was used, and his method of procedure followed closely, although it was found eventually more convenient to add the calcium oxide in small quantities at a time, so as to prevent the formation of the hard masses. It was found when hydrogen sulphide was passed into 1 part of calcium oxide, suspended in 4 parts of water, that the oxide completely dissolved, as observed by Divers, due presumably to the complete conversion of all the calcium oxide into hydrosulphide. For *à priori* it is exceedingly improbable that calcium oxide should dissolve in water containing hydrogen sulphide simultaneously as the hydroxide and the hydrosulphide. In order to bring further evidence on this point, a tube containing water saturated at about 13° with hydrogen sulphide was weighed, and to it was gradually added a known weight of calcium oxide, which was completely dissolved; the water evaporated by the passage of this gas was collected in a calcium chloride tube. The tube and its contents were again weighed, and the difference in weight before and after the experiment, less that of the calcium oxide added, represents the amount of hydrogen sulphide absorbed.

The following results were obtained:—

	Calcium oxide.	Hydrogen sulphide required.	Percentage.
Theory	2·5103	3·048	100
Experiment ...	2·5103	2·880	94·48

As a further confirmation the atomic ratio of the calcium to the sulphur in the resultant solution was found to be $\text{Ca} : \text{S} = 1 : 1·191$;

it is thus shown both by synthetical and analytical processes that the calcium oxide is practically converted entirely into calcium hydrosulphide. The same point was more fully investigated in a repetition of the above experiment. 20 c.c. of water were saturated with hydrogen sulphide at the ordinary temperature; the results are given in the following table.

I. Weight of water + H ₂ S + CaO added.	II. Gain.	III. Weight of water collected.	IV. Total gain.	V. Lime added.	VI. Difference of IV - V = H ₂ S absorbed.	VII. Percentage proportion of that required by theory.
20·0272	—	—	—	—	—	—
22·9478	2·9206	0·0546	2·9751	1·3484	1·6258	99·41
22·9343	2·9071	0·0641	2·9675	<i>nil</i>	—	—
25·9416	5·9144	0·0934	6·0078	2·7368	3·271	95·41
27·9874	7·9602	0·14	8·0011	3·7450	4·2561	94·01
30·1256	10·0904	0·1779	10·2643	4·7311	5·5332	94·85

These results show that even if the solution is comparatively strong, nearly the theoretical proportion of hydrogen sulphide is absorbed. Thus, both by the dry and wet method, calcium oxide is completely converted into sulphide or hydrosulphide as the case may be. The molecular combinations of calcium and sulphur described by Folkard (*vide supra*) are in all probability mixtures of calcium sulphide with unaltered oxide.

It will be remembered, in connection with calcium hydrosulphide, that it has been proposed to make a solution of this substance on a large industrial scale, viz., by treating a mixture of the alkali waste and water with hydrogen sulphide; the solution is then evaporated to drive off the hydrogen sulphide, and there is formed, according to the experiments of V. Miller and Opl, a crystalline form of pure calcium hydrate, thus: $\text{Ca}(\text{SH})_2 + 2\text{H}_2\text{O} = \text{Ca}(\text{OH})_2 + 2\text{H}_2\text{S}$ (*Dingl. polyt. J.*, 253, 350, Abstr., 1884, 1442). There seems, however, to be some little doubt as to the entire practical realisation of this change.

Calcium Thicarbonate.

Lime, over which coal-gas containing hydrogen sulphide has been passed, technically known as "foul lime," is a well-known absorbent of carbon disulphide. In practice, the gas engineers have found that this absorption is best effected when the lime is moistened with water to such a degree that it can easily be moulded with the fingers; this material, when fouled, is mixed with an equal weight of slaked lime.

It has further been shown that the absorption of the carbon disulphide stops at a stage at which only one-third of the sulphide would be converted into the thiocarbonate or sulphocarbonate, if the change be assumed to be as follows:—



The product is a greyish-blue mass, in which nodules of a reddish-yellow colour are interspersed. On exposing this material for a short time to the air, it is again rendered effective for the removal of carbon disulphide.

A more minute study of the composition of the substance resulting from the action of carbon disulphide on calcium sulphide, and of the conditions of its formation, present several points of theoretical and technical importance.

Preliminary experiments were made, in which pure and dry hydrogen, saturated with the vapour of carbon disulphide by bubbling through that liquid, was passed into the lime tube containing nearly anhydrous calcium sulphide. No alteration in weight was observable even on passage for several days at the ordinary temperature, and at 45° and 60°, so that perfectly dry calcium sulphide is not the absorbent of carbon disulphide. A little water was then added to the tube, and the passage of the gas recontinued; the contents of the tube became at first pale yellow, then yellowish-red masses were observed. Treatment of the contents of the tube with cold water indicated that the red compound was soluble in water, leaving probably the calcium sulphide for the most part undissolved.

This suggested the *modus operandi*; the sulphide treated with carbon disulphide was quickly introduced into a flask filled with hydrogen, and some recently boiled cold water added. The flask was fitted with a plug through which passed two tubes bent at right angles, one of which served as an inlet for the hydrogen, while the other, or outlet tube, was connected with another similarly fitted flask. The sulphide was allowed to digest for some time in the cold, a continuous current of hydrogen being passed through the apparatus during the operation; when it appeared that the greater part of the substance was dissolved, the outlet tube of the flask was pushed down into the liquid, while the inlet tube was raised; by this means the solution was forced over by the current of hydrogen gas into the second flask, thus separating it from the undissolved sulphide without contact of air.

As a preliminary experiment, the proportion of calcium to sulphur was determined in about 1 c.c. of this liquid. The following results were obtained:—

1st portion—

Calcium oxide	=	0.101	grams
Barium sulphate	=	0.8496	„
Ratio of calcium to sulphur.	=	1 : 2.023	„

2nd portion—

Calcium oxide	=	0.157	grams
Barium sulphate	=	0.3418	„
Ratio of calcium to sulphur.	=	1 : 2.017	„

The liquid presumably does not contain the colourless calcium hydrosulphide; the ratio of calcium to sulphur = 1:2 would also be satisfied by substances having the composition CaS , CaCS_3 , or $\text{Ca}(\text{OH})_2, 2\text{CaCS}_3$, of which the latter, as the sequel will show, is the more probable.

In order to isolate the substance in question, further experiments were made in which the nearly anhydrous calcium sulphide was placed under a small quantity of water, and hydrogen, saturated with carbon disulphide vapour, passed into the mixture; the superincumbent water turned gradually to a red tint, and the solution was separated from the sulphide by the method indicated above. The liquid was then placed under the air-pump; after a few days red prismatic needles appeared, from which the adherent water was drained as far as possible, and they were again dried under the air-pump. The crystals thus obtained were exceedingly deliquescent, and on contact with air lost their red colour, and became yellow and less soluble in water. An analysis was made by the processes enumerated above.

	Found.	Calculated for $\text{Ca}(\text{OH})_2, \text{CaCS}_3, 7\text{H}_2\text{O}$.
Calcium.....	22.68	22.99
Sulphur.....	27.77	27.58
Carbon	3.65	3.42
Water	41.90	41.42
Oxygen (by difference).	4.00	4.59
	100.00	100.00

The substance is thus a basic calcium thiocarbonate, crystallising with 7 mols. H_2O . An aqueous solution of this substance gave with hydrochloric acid a red oil, and with solutions of various metallic salts the same precipitates and colorations observed by Berzelius (*vide supra*); it was decolorised readily by passage of carbonic anhydride with formation of calcium carbonate.

In order to prepare this substance in rather larger quantities,

hydrogen gas was first blown into a solution of calcium hydrosulphide prepared by Divers' process until a considerable quantity of crystals of calcium hydroxyhydrosulphide were precipitated. An analysis of the liquid containing these crystals in suspension showed that the ratio of calcium to sulphide was a little more than 1 : 1. The hydrogen was then made to bubble through carbon disulphide, and the liquid at first turned pale yellow, while the suspended crystals appeared to dissolve. But after a time the liquid became nearly solid from formation of a yellow crystalline substance. Hydrogen sulphide was evolved continuously throughout the process, a result in accordance with the observations of gas engineers that the passage of coal-gas containing carbon disulphide over damp foul lime caused the evolution of hydrogen sulphide, which is absorbed by a so-called check box containing damp ferric oxide. This was drained as far as possible from the mother-liquor, washed twice with freshly-distilled water, and then dried in a vacuum. The following results were—

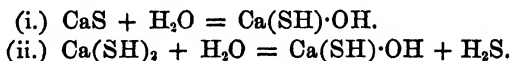
	Found.	Calculated for $2\text{Ca}(\text{OH})_2, \text{CaCS}_3, 10\text{H}_2\text{O}$.	Calculated for $10\text{Ca}(\text{OH})_2, 6\text{CaCS}_3, 50\text{H}_2\text{O}$.
Calcium....	25.14	25.20	25.12
Sulphur....	22.31	20.17	22.73
Carbon	2.75	2.52	2.82
Water.....	44.04	45.38	43.10
Oxygen (by difference)	5.76	6.73	6.33
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

The compound is thus probably $2\text{Ca}(\text{OH})_2, \text{CaCS}_3, 10\text{H}_2\text{O}$, containing a slight excess of calcium thiocarbonate; it resembled in appearance and properties the basic calcium thiocarbonate described by Walker (*vide supra*).

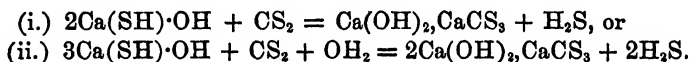
On a repetition of these latter experiments, the same succession of phenomena was observed; at first, on passage of the hydrogen with carbon disulphide vapour into the solution of calcium hydrosulphide, there separated out the white crystals of calcium hydroxyhydrosulphide accompanied by a copious evolution of hydrogen sulphide; on continuing the passage of the gas the crystals became yellow, and as the liquid turned to the consistency of a paste, about four times its volume of water was added, and the passage of the gas continued. Then there separated out the yellow crystalline substance noticed above, which subsequently dissolved to form the red liquid, yielding on evaporation in a vacuum the long red prismatic needles obtained in the former experiments. There was also slow evolution of hydrogen sulphide throughout the latter part of the experiment.

A sufficient quantity was not obtained for analysis, but the solution agreed in all its properties with former solutions and with those described by Berzelius.

From these results some conclusions can be drawn regarding the particular sulphur compound of calcium which is effective in the removal of carbon disulphide from the coal-gas. For, firstly, dry calcium sulphide does not, but moist calcium sulphide does absorb carbon disulphide; secondly, the conversion of calcium hydrosulphide into the hydroxyhydrosulphide precedes the absorption of any appreciable quantity of carbon disulphide; and thirdly, calcium hydroxyhydrosulphide suspended in water absorbs carbon disulphide. Thus the last-named substance is the absorbent formed either (i) from calcium sulphide, (ii) from calcium hydrosulphide, in accordance with the equations—



As the evolution of hydrogen sulphide is always concomitant with the absorption of carbon disulphide, and a basic calcium thiocarbonate is the resultant, the change can in all probability be represented as follows:—



This result would be in accordance with Rose's experiments (*vide supra*), which showed that the products formed by heating calcium sulphide with water were calcium hydroxyhydrosulphide and hydroxide, both of which would take part in the formation of the basic calcium thiocarbonate.

Further experiments showed that the material obtained by passing the vapour of carbon disulphide into calcium sulphide was partially decomposed with evolution of carbon disulphide by the passage of hydrogen sulphide, a result in accordance with the observations of the gas engineers, who have noticed that as the quantity of hydrogen sulphide passing into the calcium sulphide purifier was greater or less, the efficiency of the purifier was inversely diminished or increased (cf. Jones, "On the Purification of Coal-gas:" *Proc. Inst. C.E.*, 61, Part ii). The author is continuing investigations regarding the effective value of calcium sulphide for the removal of carbon disulphide, with especial reference to the purification of coal-gas.

Summary.—The main points of the above paper are as follows:—

(I.) By the action of hydrogen sulphide on solid calcium hydroxide

there is formed a calcium monosulphide in accordance with the equation $\text{Ca(OH)}_2 + \text{H}_2\text{S} = \text{CaS} + 2\text{H}_2\text{O}$.

(II.) By the action of hydrogen sulphide on calcium hydroxide in aqueous solution there is formed calcium hydrosulphide in accordance with the equation $\text{Ca(OH)}_2 + 2\text{H}_2\text{S} + x\text{Aq} = \text{Ca(SH)}_2 + 2\text{OH}_2 + x\text{Aq}$.

(III.) Calcium hydroxyhydrosulphide, $\text{CaSH}\cdot\text{OH}$, absorbs carbon disulphide with formation of unstable basic calcium thiocarbonates, decomposed slowly by hydrogen sulphide, and readily by carbonic anhydride.

In conclusion, the author wishes to return his best thanks to Mr. Vernon Harcourt for much valuable assistance and advice in the course of the inquiry.

LVI.—On the Sulphides of Titanium.

By T. E. THORPE, F.R.S.

ANALOGY points to the possible existence of at least three sulphides of titanium, corresponding respectively to the oxides TiO , Ti_2O_3 , and TiO_2 . Of these, titanium disulphide, TiS_2 , has long been known; it was discovered by Heinrich Rose, who obtained it in the form of brass-yellow lustrous scales, somewhat resembling mosaic gold, by strongly igniting titanium dioxide in a stream of carbon disulphide. Rose attempted to determine the atomic weight of titanium by means of this compound, but the results were unsatisfactory, owing to the difficulty of preparing the sulphide free from admixed oxide.

Titanium disulphide was also prepared by Ebelmen (*Ann. Chim. Phys.* [3], 20, 285), by passing the mixed vapours of titanium tetrachloride and sulphuretted hydrogen through a glass tube heated to dull redness.

In the course of an investigation on the atomic weight of titanium, the results of which have already appeared in the Transactions of the Society (this vol., p. 108), I made several attempts to prepare the disulphide by Rose's and by Ebelmen's methods, in the hope that it would constitute a suitable substance for the purpose of an atomic weight determination. In this I was not more successful than Rose had been; I varied the details of the experiments in several particulars, but without being able to obtain a product of perfectly uniform composition. These attempts, although failing to afford a satisfactory process for the determination of the atomic weight of the element,

led on further investigation to the discovery of two sulphides of titanium, corresponding to the sesquioxide Ti_2O_3 , and the monoxide TiO .

Titanium Sesquisulphide.—A small and known quantity of finely powdered titanium dioxide was placed in a porcelain boat within a porcelain tube, which could be heated to bright redness in one of Fletcher's tube-furnaces. A steady stream of sulphuretted hydrogen generated from antimony sulphide and hydrochloric acid, and most carefully dried by passing through oil of vitriol, was allowed to bubble through well-dried carbon disulphide, placed in a distilling flask, and surrounded by tepid water, and the vapours passed through the porcelain tube. After the passage of the gas had been continued for some time the tube was gradually heated to redness, and the heat maintained for one and a half hours at the highest temperature which the furnace would afford with the maximum gas supply and a full blast. The tube was allowed to cool slowly whilst the current of gas passed uninterruptedly through the apparatus. When quite cold, the boat was withdrawn. Its contents were apparently unchanged, and the weight was the same to within a few tenths of a milligram.

The experiment was repeated, but with this difference, that no pains were taken to dry the sulphuretted hydrogen or the carbon disulphide. About a gram of the pure and finely powdered oxide was placed in the boat, and the whole was heated as before for about two hours. *The product in the boat was a greenish-black powder*, altogether dissimilar from titanium disulphide in appearance. This substance is *titanium sesquisulphide*, Ti_2S_3 , as the following data show :—

Preparation I. 1.0303 gram TiO_2 gained in weight, on treatment as above, 0.2132 gram, or 20.69 per cent.

Preparation II. 1.2816 gram TiO_2 gained 0.2587 gram, or 20.19 per cent.

Preparation III. 1.4731 gram TiO_2 gained 0.3206 gram, or 21.96 per cent.

The gain in weight attending the conversion of titanium oxide into the sesquisulphide is 20 per cent. By heating the sesquisulphide at a lower temperature in the mixed vapours of carbon bisulphide and sulphuretted hydrogen, it may be gradually converted into the disulphide; hence it is difficult to obtain the substance free from the latter compound.

In order to analyse it, a small portion was heated with red fuming nitric acid, the oxidation being assisted towards the end by the addition of a few crystals of potassium chlorate. When fully oxidised, the solution was diluted with water, and the titanate precipitated

by ammonia as hydrate, boiled and filtered, the sulphuric acid being precipitated from the filtrate as barium sulphate.

0.3263 gram Ti_2S_3 gave 0.2589 gram TiO_2 , and 1.2297 gram $BaSO_4$.

	Calculated.	Found.
Ti.....	50.0	47.61
S	50.0	51.7
	<hr/> 100.0	<hr/> 99.31

The discrepancy is due to the admixture of the disulphide, which contains upwards of 57 per cent. S.

Titanium Monosulphide.—This substance was obtained by heating the sesquisulphide in a current of dry hydrogen gas, freed from oxygen by passage through an alkaline solution of pyrogallol. The same substance has also been obtained by von der Pfordten (*Ber.*, 17, 727), by heating the disulphide in a similar manner. It is a black powder, which is but slowly acted on by nitric acid or by aqua regia.

0.8216 gram Ti_2S_3 lost on heating in hydrogen for three hours, 0.1292 gram, or 16 per cent.

The calculated loss on converting Ti_2S_3 to TiS is 16.6 per cent. On analysis—

3.324 gram gave 0.9352 gram $BaSO_4$.

	Theory	Found.
S	40.0	39.2

The analogy between the sulphides and oxides of titanium is therefore complete, and for each oxide there is a corresponding sulphide.

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LVII.—Colorimetric Method for Determining Small Quantities of Iron.

By ANDREW THOMSON, M.A., B.Sc., Student in the Chemical Laboratory of University College, Dundee.

THIS method, which I have worked out at the suggestion of Professor Carnelley, is meant to supply an accurate and ready means of estimating minute quantities of iron in the presence of large quantities of other metals, and more especially in alloys. Besides being accurate and easily applied, it is extremely sensitive, for by its means it is possible to detect and estimate so small a quantity as

1 part of iron in 50,000,000 parts of water, whilst the addition of ~~1000000~~ of a gram of iron to the reagent produces a distinct local coloration. It is, therefore, more sensitive than any other known colorimetric method, for the Nessler test, which has hitherto been considered the most delicate, allows of the estimation of 1 part of ammonia in but 20,000,000 parts of water.

The process depends upon the well-known blood-red coloration produced by the action of ferric salts on potassium thiocyanate, and has been found to be almost universally applicable; silver and copper, and in some cases cobalt, being the only common metals that interfere with its action.*

To carry out the method, the following materials are required —

1. *A standard solution of iron*: this is prepared by dissolving 0.7 gram of ferrous ammonium sulphate in water, and after the addition of 5 c.c. of dilute sulphuric acid, the iron is converted into ferric salt by means of potassium permanganate, and the whole made up to 1 litre, 1 c.c. = 0.0001 gram of Fe. In the case of metals that are precipitated by sulphuric acid—e.g., barium and lead—a standard solution of ferric chloride is employed, obtained by dissolving 0.1 gram of piano-wire in hydrochloric acid, and after treatment with potassium permanganate diluting to 1 litre, 1 c.c. = 0.0001 gram of Fe

2. *A solution of potassium permanganate*, which should be moderately dilute, but does not require to be standardised.

3. *Dilute hydrochloric acid or nitric acid*, 1 to 5.

4. *A solution of potassium thiocyanate*, prepared by dissolving 10 grams of the crystallised salt in 250 c.c. of water.

5. *Two glass cylinders* of 150 c.c. to 200 c.c. capacity, and graduated at every 25 c.c.

The analysis is carried out as follows:—Dissolve a weighed quantity of the substance in which the amount of iron is to be determined in a suitable acid, and evaporate nearly to dryness to expel excess of acid. After slightly diluting with water, convert the iron into the ferric state by potassium permanganate, and make up the liquid to 1 litre. Into each of the two glass cylinders, pour 5 c.c. of the dilute hydrochloric or nitric acid, and 15 c.c. of the potassium thiocyanate. Then add to one (x) a measured quantity of the same } be tested. Fill up both cylinders with distilled water to the same } mark, say 100 c.c. If iron be present a blood-red coloration

* As is neutral salt known, the presence of mercuric chloride in a neutral or nearly ferric chloride instantly bleaches the red colour produced by thiocyanates with colour is not but if 5 c.c. of nitric or hydrochloric acid—1 : 5—be added, the red presence of thoyed even after standing for 15 or 20 minutes. In this case the formation of w^hee acid hinders the precipitation of mercuric thiocyanate, the causes decolorisation under ordinary circumstances

will be produced in (x), which will be dark or light according to the amount of iron present. Then run the standard iron from a burette into the other cylinder (y) until the shades of colour in the two are the same. Since 1 c.c. of the standard iron = 0.0001 gram Fe, the amount of iron present in the substance is easily calculated.

The quantity of iron in the test cylinder at one time should not require more than 2 c.c. to 3 c.c. of the standard to produce an equal shade, otherwise the colour is too deep for comparison. The presence of acids greatly increases the sensitiveness of the reaction. In order, therefore, to obviate the disturbing effect of the casual presence of any acid, the solutions are always made distinctly acid by the addition of 5 c.c. of the dilute hydrochloric or nitric acid referred to in 3. Experiment shows that the presence of even large quantities of organic matter does not affect the reaction. If the metal or metals which are in solution along with the iron forms two sets of salts, the metal should be converted into the salt corresponding to the higher oxide, *e.g.*, mercurous into mercuric, and stannous into stannic, otherwise the coloration is destroyed. It is also destroyed by even minute quantities of oxalic acid, though the presence of arsenic and phosphoric acids does not affect it, provided *there be plenty of acid present* (*cf. Watts' Dict.*, 3, 381).

The degree of accuracy of the method is shown in Tables I, II, and III, of which Table I gives the results obtained with pure solutions of iron; and Table II those got in the presence of various other metals, the salts chiefly used being the sulphates, nitrates, and chlorides. As previously stated, accurate results were also got in presence of phosphates and arsenates; Table III gives the results obtained in the presence of organic matter (tartaric acid, sugar, &c.).

TABLE I.—*Pure Solutions of Iron.*

Milligrams calculated.	Milligrams found.	Milligrams calculated	Milligrams found.
0.031	0.030	0.314	0.320
0.045	0.042	0.392	0.360
0.062	0.060	0.440	0.440
0.078	0.080	3.130	3.000
0.094	0.090	11.270	12.000
0.120	0.120	31.280	31.500
0.157	0.150	56.250	55.000
0.220	0.220	101.920	98.670

As an example of the actual application of the method, the quantity

TABLE II.—*Iron in Presence of other Metals.*

Metal present.	Proportion of metal to 1 of Fe.	Milligrams calculated.	Milligrams found.
Lead	164	1.28	1.32
"	1702	1.12	1.09
Mercury	224	0.46	0.44
"	1090	2.49	2.48
Cadmium	640	0.63	0.61
"	1050	1.56	1.60
Bismuth	235	0.24	0.23
"	940	1.20	1.25
Arsenic	375	0.42	0.44
"	1762	1.60	1.52
Tin	896	0.656	0.688
"	1079	1.360	1.352
Antimony	156	0.448	0.440
"	259	0.656	0.688
Nickel	214	0.288	0.280
"	239	0.500	0.520
Cobalt	74	0.584	0.602
"	153	2.800	2.747
Manganese	140	0.798	0.792
"	557	2.133	2.160
Aluminium	82	0.570	0.520
"	106	1.290	1.260
Zinc	339	0.313	0.340
"	550	0.772	0.720
Strontium	291	0.600	0.580
"	375	1.166	1.200
Barium	909	0.213	0.232
"	1718	0.440	0.432
Calcium	513	0.300	0.316
"	783	1.116	1.090
Magnesium	144	0.300	0.316
"	301	1.430	1.380
Sodium and potas- sium	{ Na = 230 } { K = 345 }	0.410	0.440
Sodium and potas- sium	{ Na = 472 } { K = 708 }	0.806	0.816

TABLE III.—*Organic Matter.*

Name of substance.	Proportion to 1 of Fe.	Milligrams calculated.	Milligrams found.
Sugar	398	0.253	0.280
"	967	1.566	1.630
Tartaric acid	454	0.400	0.440
"	1035	0.660	0.614
"	2884	1.040	1.120

of iron in a sample of commercial nickel wire was determined as follows:—

0.493 gram of the wire was dissolved in nitric acid, evaporated to expel excess, and made up to $\frac{1}{4}$ litre.

15 c.c. of nickel solution required 3.34 c.c. of standard iron to produce the same colour with potassium thiocyanate:

∴ 15 c.c. of nickel solution	= 0.000334 gram Fe.
∴ 250 " "	= 0.00556 "
	= 1.13 per cent. Fe in nickel wire.
A second experiment gave. .	= 1.16 " "

As a further check 0.163 gram of the same wire was dissolved in hydrochloric acid and oxidised by potassium permanganate instead of nitric acid, and the iron determined as before, giving 1.15 per cent. of Fe.

Similar experiments were made with a sample of tin. In one case 0.023 per cent., and in another 0.021 per cent. of Fe were obtained.

The experiments in the case of nickel show that the results are the same whether the oxidising agent used be nitric acid or potassium permanganate, though in most cases it is preferable to use the latter, on account of the ease with which it can be manipulated.

From its almost universal applicability, simplicity, accuracy, and the great celerity with which it can be applied, this process for estimating small quantities of iron should be found extremely useful.

LVIII.—*On the Constitution of the Haloid Derivatives of Naphthalene.* (Fourth Notice.)

By RAPHAEL MELDOLA, Professor of Chemistry in the Finsbury Technical College; City and Guilds of London Institute.

Introduction.

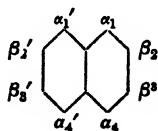
ALTHOUGH during the last few years many investigators have directed their attention to the development of our knowledge of the naphthalene-derivatives, the laws of substitution in this interesting and important hydrocarbon are as yet very imperfectly worked out as compared with those governing the introduction of various substituents into the less complicated benzene molecule. This comparative deficiency in our knowledge is the less remarkable, however, when it is considered how much more complicated the isomerism of the benzene-derivatives becomes by the duplication and condensation of the closed ring.

Thus, while only three di-derivatives of benzene are theoretically possible, whether the substituting atoms (or groups) are similar or dissimilar, the generally received formula of naphthalene indicates the possible existence of 10 di-derivatives with similar substituents, and no less than 14 di-derivatives with dissimilar substituents.

But quite apart from the theoretical importance attending the investigation of the laws of substitution in the naphthalene-derivatives, the study of these compounds is much facilitated practically, owing to their technical importance. Such materials as β -naphthol, α -nitronaphthalene, α -dinitronaphthol, α - and β -naphthylamine, &c., are now industrial products, and can be obtained in any quantity in a state of almost chemical purity.

Among the numerous researches on naphthalene compounds which have been published since my last communication on this subject (this Journal, 43, 1883, Trans, 1), I will here only call attention to the excellent memoir by Guareschi, which appeared soon after the publication of the foregoing paper ("Ricerche sui Derivati della Naftalina," Turin, 1883; reprinted from the *Mem. d. R. Accad. d. Sci. Torino*, Ser. II, 25). In this paper, the author establishes, amongst a very large number of other facts, the interesting result that the nitrobromonaphthalene obtained by brominating α -nitronaphthalene is different in constitution from that obtained by Jolin (*Bull. Soc. Chim.*, 28, 1877, 514) by nitrating α -bromonaphthalene. In brominating α -nitronaphthalene it appears indeed that the bromine-atom enters the unsubstituted ring, a fact which renders it necessary to observe caution before accepting the general conclusion that the behaviour of the NO_2 -group and the halogens is the same in all cases of substitution. It is highly probable that in the case of hydrocarbons which readily form additive compounds with the halogens, such compounds are in the first place always formed, and this may account for the different results obtained, according as the NO_2 -group or the halogen is first introduced into the naphthalene molecule.

In the case of the di-derivatives of naphthalene, which have hitherto received the largest amount of attention, the laws of substitution appear to present many analogies to those observed in the benzene series. The present researches have been undertaken chiefly with the object of passing from di-derivatives of known constitution to the less known tri-derivatives. Throughout the paper, the following formula will be employed:—



I. BROMINATION OF NITRACENAPHTHALIDES.

Pure α -acenaphthalide was dissolved in glacial acetic acid, and nitrated in the cold by means of the theoretical quantity of fuming nitric acid (1.5 sp. gr.), according to Andreoni and Biedermann's method (*Ber.*, 6, 342). The liquid was decanted from the crystalline crust, and mixed with a large bulk of water, the portion thus precipitated from the mother-liquor being reserved for the separation of γ -nitracenaphthalide, which, according to Liebermann and Dittler (*Ber.*, 7, 245), is contained in the acetic acid solution. The crystalline deposit was purified by crystallisation from glacial acetic acid and alcohol successively.

The researches of Liebermann and his pupils have shown that the nitracenaphthalide first deposited from the acetic acid liquor consists of two modifications having nearly the same melting point (171°), and a more recent investigation by Lellmann (*Ber.*, 17, 109) renders it probable that another modification is also contained in this fraction, thus giving four, or possibly only three, nitracenaphthalides as the result of the action of fuming nitric acid on α -acenaphthalide in cold acetic acid solution. Of these modifications the most abundant is paranitracenaphthalide, $C_{10}H_6 \begin{smallmatrix} \text{NHAc} \dots \alpha_1 \\ \text{NO}_2 \dots \alpha_4 \end{smallmatrix}$; the ortho-compound,



being present in smaller quantity, whilst Lellmann's modification, of which the constitution is at present unknown, appears to be formed only in very small quantity.

β_2 -Brom- α_4 -nitro- α_1 -acenaphthalide; m. p. 225° .

The purified crystalline mixture of nitro-compounds obtained in the manner described was dissolved in about six times its weight of glacial acetic acid, and bromine (one molecular proportion) added to the cold solution. After standing for about 18 hours, whitish silky needles had separated out, and on agitating the contents of the flask a further separation took place, causing the mass to become semi-solid. It was observed that the whole of the bromine was never absorbed. The crystalline pulp was well drained on a filter, washed with water, and purified by three or four crystallisations from alcohol, the substance being finally obtained in the form of long fibrous pale ochreous needles, having a sharply defined melting point of 225° . This is the bromonitracenaphthalide, to the discovery of which attention has already been directed in a previous paper (this Journal, 43, Trans.,

1883, 9), and which is isomeric with the compound (m. p. 230°) obtained by Liebermann and Scheiding (*Ber.*, 8, 1108) by nitrating parabromacenaphthalide.

β₂-Brom-α₄-nitro-α₁-naphthylamine; m. p. 197°.

The hydrolysis of the foregoing bromonitracenaphthalide is most readily effected by dissolving the substance in a considerable quantity of strong sulphuric acid, and then gradually diluting with water, taking care not to add so much water as to cause precipitation. The heat developed by the dilution of the acid was quite sufficient to effect the removal of the acetyl-group, and the solution when cold was stirred into a large bulk of cold water; this caused the bromonitronaphthylamine to separate out as a bright orange, flocculent precipitate, which was collected, washed free from acid, dried, and crystallised from toluene. It was thus obtained pure in the form of large orange needles, melting sharply at 197°.

0.2557 gram burnt with lime gave 0.1820 gram AgBr.

Theory for C ₁₀ H ₅ Br(NO ₂)·NH ₂ .	Found.
Br 29.96 per cent. Br.	30.29

This is the second known bromonitronaphthylamine, and is isomeric with that of Liebermann and Scheiding (*Ber.*, 8, 1108, and *Ann. Oh.*, 183, 258), melting at 200°, and obtained by saponifying the nitro-derivative of parabromacenaphthalide. It is readily soluble in hot alcohol, the benzene hydrocarbons, and chloroform, but only slightly soluble in carbon disulphide. It possesses but very feeble basic properties, dissolving in sulphuric acid only when the acid is concentrated, and separating unaltered on the addition of water. By repeated evaporation with dilute nitric acid, it yields phthalic acid in considerable quantity. Several attempts were made to obtain a monobromonaphthaquinone by reducing this bromonitronaphthylamine and oxidising the resulting diamidobromonaphthalene, but the experiments, although varied in many ways, have hitherto yielded negative results.

β₂-Brom-α₄-amido-α₁-acenaphthalide.

The preceding bromonitracenaphthalide (m. p. 225°) was dissolved in glacial acetic acid, and the cold solution agitated with zinc-dust. The excess of zinc was removed by filtration, and the filtrate diluted with water, when the amido-compound separated out as a white gelatinous precipitate. The substance was collected, washed, and dried, but could not be obtained in a crystalline state, owing to the tendency which it has to separate from its solutions in the form

of a jelly. It possesses no basic properties, and is remarkably stable, the acetyl-group not being removed after boiling for eight hours with a syrupy solution of caustic soda. Strong sulphuric acid also fails to saponify it. The dried substance has a melting point of about 222° , and is very sparingly soluble in boiling toluene, but somewhat more soluble in alcohol. It dissolves in boiling water, and separates in a gelatinous state on cooling.

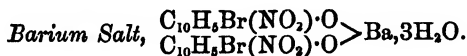
β_2 -Brom- α_1 -nitro- α_1 -naphthol; m. p. 136° .

The bromonitracenaphthalide previously described is readily soluble in dilute alkalis, the hydrogen-atom of the acetamido-group being replaceable by metals, owing to the acid character of the molecule. On boiling for some time with strong caustic soda solution, however, the acetamido-group is displaced, ammonia being given off, and the sodium-derivative of bromonitronaphthol formed, the latter separating out as a deep red crystalline deposit. After recrystallisation from boiling water, in which it is not very soluble, it was obtained pure in the form of small red needles, having the formula—



- I. 0.3668 gram, dried at 120 — 130° till constant in weight, lost 0.0214 gram.
- II. 0.3438 gram, dried in a vacuum over sulphuric acid, gave 0.0836 gram Na_2SO_4 .
- III. 0.2596 gram, dried at 120 — 130° , and burnt with lime, gave 0.1666 gram AgBr .

	Theory.	Found.
Br	27.58 (anhydrous salt)	27.31 p. c.
Na	7.46	7.88 „
H_2O	5.84	5.83 „



On adding a solution of barium chloride to a hot aqueous solution of the sodium salt, the barium salt is precipitated as a red amorphous powder, insoluble in boiling water. When dry, the salt burns slowly on ignition, giving off dense orange fumes.

- I. 0.3120 gram, dried at 150 — 160° till constant in weight, lost 0.0226 gram.
- II. 0.2891 gram, dried at 150 — 163° , gave 0.10 gram BaSO_4 .
- III. 0.2090 gram, dried in a vacuum over sulphuric acid, and burnt with lime, gave 0.1090 gram AgBr .

	Theory.	Found.
Ba	20·41 (anhydrous salt)	20·33 p. c.
Br	22·06	22·19 „
H ₂ O	7·44	7·24 „

Bromonitronaphthol was obtained by decomposing a hot solution of the sodium salt with hydrochloric acid. A bright yellow flocculent precipitate was thrown down, which, after being collected, washed, and crystallised from alcohol, formed silky, yellow needles, fusing at about 136°, and at the same time blackening and decomposing. This compound is isomeric with the bromonitronaphthol of Biedermann and Remmers (*Ber.*, 7, 538), which melts at 142°. A bromine determination gave the following results:—

0·2964 gram burnt with lime gave 0·2080 gram AgBr.

	Theory for C ₁₀ H ₅ Br(NO ₂)·HO.	Found.
Br	29·85 per cent.	29·86

When the glacial acetic acid solution of the bromonitronaphthol is boiled for some time, decomposition takes place, with the evolution of bromine vapour.

Of the other salts of this compound, the following have been prepared:—

Ammonium Salt.—Orange needles, becoming yellow on drying at 100°. Much more soluble in water than the potassium or sodium salt.

Calcium Salt.—Red amorphous powder, insoluble in hot or cold water.

Silver Salt.—Obtained by decomposing a hot solution of the ammonium salt with silver nitrate. A bright orange precipitate consisting of microscopic needles; insoluble in hot water.

Copper Salt.—Obtained by decomposing a hot solution of the ammonium salt with cupric sulphate. A dull red flocculent precipitate, insoluble in hot water.

Bromonitronaphthol Methyl Ether.—Prepared by acting on the silver salt with methyl iodide. After crystallisation from alcohol, it was obtained in the form of silky, pale yellow needles, melting at 114—115°. The formula of this compound is C₁₀H₅Br(NO₂)·OCH₃.

When oxidised in an alkaline solution with potassium permanganate this bromonitronaphthol furnishes a considerable quantity of phthalic acid.

Bromination of Liebermann's γ-Nitracenaphthalide.

In the mother-liquors decanted from the crystalline deposit obtained by nitrating α-acenaphthalide in acetic acid solution, there is con-

tained, as already stated, a nitracenaphthalide, which Liebermann and Dittler found to have a melting point of 189° (*Ber.*, 7, 245). This modification appeared to be chemically identical with the α -(para)-acenaphthalide, inasmuch as its derivatives were found to be identical with those of the latter modification. More recently this γ -nitracenaphthalide has been re-examined by Lellmann (*Ber.*, 17, 109), who confirms Liebermann's conclusions as to the identity of the derivatives of this modification with those of α -nitracenaphthalide. The results of both these chemists are here given:—

Derivative.	α -Nitracenaphthalide.	γ -Nitracenaphthalide.
Nitronaphthalene	58° m. p.	58° m. p.
Naphthaquinone	125 "	125 "
Nitronaphthylamine	190 "	190 "
Nitronaphthol	164 "	164 "
Benzoylnitronaphthalide	224 "	224 "
Benzoylnaphthylenedi- amine	186 "	186 "

Lellmann found that γ -nitracenaphthalide when pure melts at 187° , and having had occasion to prepare some quantity of this substance, I can confirm this statement. By acting on α -nitronaphthylamine with acetic anhydride, Lellmann obtained a nitracenaphthalide, melting at 187° , and apparently identical with the γ -modification, from which he concludes that the latter is actually α -nitracenaphthalide, this result being in accordance with the fact that the derivatives of the two modifications are identical.

It appeared of interest in connection with the foregoing results to study the action of bromine on γ -nitracenaphthalide in order to see whether the identity of the mono- and di-derivatives with those of α -nitracenaphthalide extended also to the tri-derivatives of the γ -modification. In order to conduct the experiment, the crude product precipitated by water from the acetic acid mother-liquors was crystallised repeatedly from alcohol, till it had a constant melting point of 187° . Some of the pure γ -nitracenaphthalide thus obtained was dissolved in about six times its weight of glacial acetic acid, and the theoretical quantity (one molecular proportion) of bromine added to the solution. Nothing had separated out after standing for two days, and the bromine was apparently still unabsorbed. The solution was therefore diluted with water, and allowed to stand for another day, by which time the free bromine had practically disappeared. The precipitate was collected, washed with water, and repeatedly crystallised from alcohol, numerous crystallisations being necessary before a substance of constant melting point could be isolated. A small quantity of a compound melting at 224 — 226° was finally obtained, and this appeared

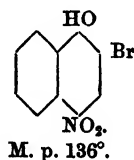
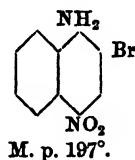
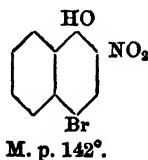
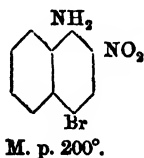
to be identical with the bromonitracenaphthalide previously described, although the melting point was by no means sharp, owing to the presence of some impurity which could not be separated by crystallisation. From this it appears that γ -nitracenaphthalide furnishes the same bromine-derivative as the α -modification, but the experiment also shows that the bromination takes place less readily, as it could not be effected in an acetic acid solution of the same strength as that in which the α -modification is readily attacked.

In order to confirm this result, a further quantity of the γ -compound was brominated in about 3 to 4 times its weight of acetic acid, but the substance which crystallised out after standing for one day was found to be unaltered γ -nitracenaphthalide, giving α -nitronaphthol (m. p. 163—164°) on hydrolysis by boiling caustic soda.

The quantity of γ -nitracenaphthalide obtained in the nitration process employed is very small, and want of material has prevented me from further investigating this modification, but as the result of the present experiments it seems to me that it is a body well worthy of detailed study. It is certainly an interesting circumstance that of two compounds yielding identical derivatives, one should be more difficult to brominate than the other. If, as is not improbable, we have here a case of physical isomerism, Lellmann's conversion of α -nitronaphthylamine into an acetyl-derivative, having the melting point (187°) of γ -nitracenaphthalide, may simply indicate that under the action of acetic anhydride, α -nitronaphthylamine is converted into the acetyl-derivative of its physical isomeride.

Constitution of the foregoing Compounds.

It appeared probable, on general grounds, that the bromonitronaphthylamine and bromonitronaphthol previously described were related to the corresponding modifications of Liebermann and Scheiding (m. p. 200°), and Biedermann and Remmers (m. p. 142°), in the following manner:—



The above formulæ for the new modifications were rendered probable from the circumstance that they both furnished phthalic acid on oxidation, and were thus shown to be homonuclear derivatives. The nitracenaphthalides submitted to the action of bromine consist

essentially of the para- and ortho-modifications, and previous experience of the laws of substitution in the naphthalene series had shown that substitution takes place much more readily in para- than in ortho-derivatives. Thus, as shown in a previous paper (this Journal, **43**, Trans., 1883, 8), orthobromo- β -acenaphthalide is not further attacked by bromine in the cold in acetic acid solution, and experiments made with the object of nitrating this modification, although varied in many ways and tried with acids of various strengths, also served to show that the NO_2 -group could not be readily made to enter this ortho-compound. On the other hand, Liebermann has shown that parabromacenaphthalide ($\text{Br} : \text{NHAc} = \alpha_1\text{-}\alpha_4$) is very easily nitrated. It appeared most probable, therefore, that of the mixed ortho- and para-nitracenaphthalides the latter would alone be attacked by bromine in cold glacial acetic acid solution, and this view was strengthened by the large quantity of the brominated product obtained (paranitracenaphthalide being the chief product of the original nitration), as well as by the circumstance that the whole of the bromine was never absorbed, although the theoretical proportion was always carefully employed. It will be shown subsequently that this view of the constitution of these modifications is completely established by the conversion of the resulting nitrobromonaphthalene into *meta*-dibromonaphthalene.

From the point of view that the present compounds are the analogues of Liebermann's bromonaphthylamine and bromonitronaphthol, it became desirable to determine more precisely than had hitherto been done the constitution of these latter modifications, as all that is at present known with respect to them is that the three substituents are in the same nucleus, and that the NO_2 -group is consequently in one of the β -positions. This latter group can thus be only in the ortho- or meta-position with respect to the acetamido-group; if in the former, as appeared most probable by analogy with the benzene series, reduction would furnish an anhydro-base, and this was found to be the case by experiment.

Parabromacenaphthalide was dissolved in glacial acetic acid, and nitrated by warming with nitric acid (sp. gr. 1.42) to about 70—80° for half an hour. The substance was obtained pure after one crystallisation from alcohol. The reduction of the nitro-compound was effected in alcoholic solution by means of zinc-dust. After filtration, the alcohol was evaporated, the residue washed with water to remove zinc salts, and the base liberated by ammonia. The free base could not readily be obtained in a crystalline form; it was freely soluble in alcohol and acetone, and insoluble in benzene, toluene, or petroleum. By allowing the acetone solution to evaporate slowly, small nodules separated having a melting point of about 202°, but com-

mencing to soften before this temperature. The salts generally have a great tendency to gelatinise, but the nitrate was at length obtained in the form of white silky needles by crystallisation from absolute alcohol. A preliminary test showed that the substance contained bromine, and analysis of the nitrate led to the conclusion that the base was ethenylbrom- $\alpha\beta$ -naphthylenediamine :—



- I. 0.1520 gram burnt with CaO gave 0.0872 gram AgBr.
 II. 0.2595 gram burnt with CaO gave 0.1505 gram AgBr.
 III. 0.1829 gram burnt with lead chromate gave 0.2969 gram CO_2 and 0.0569 gram H_2O .

Theory for $\text{C}_{12}\text{H}_9\text{BrN}_2, \text{HNO}_3$.	Found.		
	I.	II.	III.
C.....: 44.44 p. c.	—	—	44.27 p. c.
H 3.08 „	—	—	3.45 „
Br 24.69 „	24.41	24.68	— „

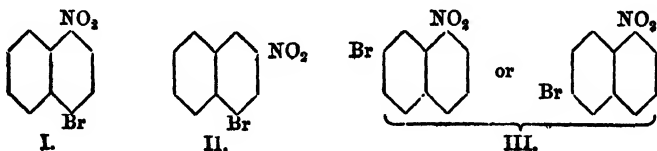
II. NITROBROMONAPHTHALENES.

In order to throw further light upon the constitution of the foregoing tri-derivatives, it became of interest to eliminate the NH_2 -group, and to obtain the corresponding nitrobromonaphthalenes, bromonaphthylamines, and dibromonaphthalenes.

Up to the present time, the three following nitrobromonaphthalenes have been obtained :—

- I. M. p. 85° . Obtained by Jolin by nitrating α -bromonaphthalene (*Bull. Soc. Chim.*, **28**, 514). Guareschi gives the melting point of this modification as 83 — 84° .
 II. M. p. 131 — 132° . Obtained by Liebermann and Scheiding by displacing the NH_2 -group in bromonitronaphthylamine (m. p. 200°) by hydrogen (*Ber.*, **8**, 1108).
 III. M. p. 122.5° . Obtained by Guareschi by brominating α -nitronaphthalene (*Mem. d. R. Accad. d. Sci. d. Torino*, Ser. II, **35**).

The constitution of these three modifications is shown in the following formulæ :—



α_1 -Nitro- β_2 -bromonaphthalene; m. p. 131°.

A fourth nitrobromonaphthalene has been obtained from the bromonitronaphthylamine previously described, by displacing the NH_2 -group in it by hydrogen, by means of the diazo-reaction. The following method has been found to work so successfully in all the NH_2 -displacements effected in the course of the present research that it may be of use to give the details, more especially as these diazo-reactions are liable to give rise to tarry and unsatisfactory products, unless the most scrupulous precautions are observed at every stage.

The bromonaphthylamine was dissolved in a considerable excess of strong sulphuric acid, the solution diluted with a small quantity of water, and the necessary quantity of sodium nitrite added in small quantities in the solid state to the well-cooled solution. When diazotised, the solution is poured in a thin stream into about 2—3 times its bulk of alcohol; nitrogen is given off with a strong effervescence, and the mixture becomes warm enough to complete the reaction without any further heating. On mixing with a large bulk of water and allowing to stand, the nitrobromonaphthalene separates out as a mass of whitish needles, which are purified by crystallisation from alcohol. By using an excess of strong sulphuric acid, and observing the precautions laid down, ordinary methylated spirit can be employed for decomposing the diazo-sulphate in these reactions, and gives just as good results as absolute alcohol.

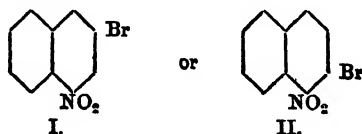
This new nitrobromonaphthalene forms pale straw-coloured needles, soluble in alcohol, benzene, &c., and melting at 131°.

0.2364 gram burnt with lime gave 0.1760 gram (AgBr).

	Theory for $\text{C}_{10}\text{H}_6\cdot\text{NO}_2\cdot\text{Br}$.	Found.
Br	31.74 per cent.	31.68

In order to determine the constitution of this modification, it was converted into the corresponding dibromonaphthalene, the constitution of the various modifications of this latter compound having been established with some completeness in the course of former investigations.

The bromonitronaphthylamine from which the present nitrobromonaphthalene is derived contains the three substituents in the same nucleus, as has already been shown by the production of phthalic acid from it by oxidation. Thus, two formulæ only are possible for the present modification;—



Formula I would furnish metadibromonaphthalene (*Ber.*, 12, 1962), whereas formula II would give orthodibromonaphthalene (this Journal, 43, Trans., 5). The decision between the formulæ was therefore a point of some importance, as the constitution of the bromonitronaphthylamine would at the same time be settled. The conversion was effected in the following manner:—

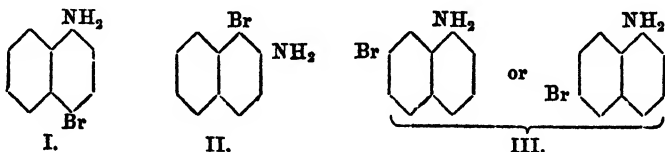
The nitrobromonaphthalene was dissolved in glacial acetic acid, and the cold solution agitated with zinc-dust. The solution of the bromonaphthylamine in acetic acid was freed from excess of zinc-dust by filtration, mixed with water and dilute sulphuric acid, well cooled, and the theoretical quantity of sodium nitrite necessary to diazotise the amine gradually added. Bromine-water in excess was then added to the solution, and on standing for about an hour the diazo-perbromide had settled out in yellow crystals. The latter were collected, washed, dried by pressure between filter-paper, and decomposed by warming with glacial acetic acid in the usual way. The crude dibromonaphthalene thus obtained was purified by repeated crystallisation from alcohol with the addition of animal charcoal, and finally proved to be identical in crystalline form and melting point (64°) with metadibromonaphthalene. Formula I is thus shown to be correct, and the constitution previously assigned to the bromonitronaphthylamine of m. p. 197° ($\beta_2\alpha_4\alpha_1$) is at the same time established.

III. BROMONAPHTHYLAMINES.

Of 14 bromonaphthylamines, theoretically possible, the three following are at present known:—

- I. M. p. 94°. Obtained by the hydrolysis of α -bromacenaphthalide (Rother, *Ber.*, 4, 850; also a paper by the author, this Journal, 43, Trans., 5).
- II. M. p. 63°. Obtained by the hydrolysis of β -bromacenaphthalide (Cosiner, *Ber.*, 14, 59; also the paper by the author, *loc. cit.*).
- III. M. p. 63–64°. By the reduction of Guareschi's bromonitronaphthalene, m. p. 122·5 (Guareschi; *loc. cit.*).

The constitution of these modifications is shown in the following formulæ:—



Two new bromonaphthylamines have been obtained in the course of the present researches, and may be here described.

α_1 -Brom- β_2 -naphthylamine; m. p. $71\cdot5^\circ$.

In his classical researches on the naphthalene series, Liebermann found (*Annalen*, 183, 225—275) that his nitrobromonaphthalene could not be reduced without at the same time eliminating the bromine-atom, β -naphthylamine being produced. According to my experiments, this statement only holds good, however, when violent reducing agents, such as tin and hydrochloric acid, are made use of; by the employment of zinc-dust and acetic acid, reduction can be effected without the removal of bromine.

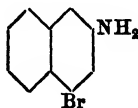
Liebermann's nitrobromonaphthalene was dissolved in glacial acetic acid, and the well-cooled solution agitated with zinc-dust, the excess of zinc filtered off, and the bromonaphthylamine precipitated from the solution by the addition of water. After several crystallisations from dilute alcohol, and finally from a mixture of benzene and petroleum, a specimen was obtained in the form of whitish needles, having a constant melting point of $71\cdot5^\circ$. and gradually reddening on exposure to the air. This bromonaphthylamine possesses but very feeble basic properties; it is extremely soluble in alcohol and benzene, and practically insoluble in boiling water. The acetyl compound was obtained by boiling the glacial acetic acid solution for a few minutes with the addition of acetic anhydride. It forms white needles which, after crystallisation from alcohol, had a constant melting point of $186\cdot5^\circ$.

0·1865 gram burnt with lime gave 0·1330 gram AgBr.

Theory for $C_{10}H_6Br\cdot NHAc$.		Found.
Br	30·30 per cent.	30·34

This bromacenaphthalide is converted into resinous products by the action of nitric acid; it readily takes up another atom of bromine with the formation of a dibromacenaphthalide which will be described subsequently.

The constitution of this bromonaphthylamine, as appears from the constitution of the bromonitronaphthylamine from which it is derived, is obviously—



This was confirmed by converting a small quantity into the corresponding dibromonaphthalene by decomposing the diazo-perbromide in

the usual way; the resulting compound was metadibromonaphthalene (m. p. 64°).

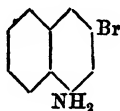
*β*₂-Brom-*α*₁-naphthylamine; m. p. 62°.

The reduction of the corresponding nitrobromonaphthalene was effected by means of zinc-dust in acetic acid solution in the manner above described. The bromonaphthylamine, after crystallisation from dilute alcohol (equal parts alcohol and water), was obtained in the form of whitish needles, melting at 62°, and soluble in all the ordinary solvents, with the exception of water. In distinction from the preceding modification, it possesses well-marked basic properties, dissolving freely in warm dilute hydrochloric acid, and being precipitated by alkalis. When pure, the acetyl compound forms white needles melting at 187°.

0.2364 gram burnt with lime gave 0.1669 gram AgBr.

Theory for C ₁₀ H ₇ Br·NH ₂ ·	Found.
Br 30.30	30.04

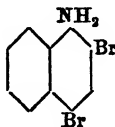
The constitution of the bromonaphthylamine is—



this formula having been established when treating of the nitrobromonaphthalene from which it is derived.

IV. DIBROMONAPHTHYLAMINES AND THEIR DERIVED DI- AND TRI-BROMONAPHTHALENES.

The only dibromonaphthylamine at present known is the one of m. p. 118—119°, described in a former paper (*Ber.*, 12, 1961), prepared by saponifying the dibromacenaphthalide obtained by the bromination of parabromacenaphthalide, and having the constitution—



The acetyl-derivatives of the preceding bromonaphthylamines, although not capable of being nitrated without destruction, readily take up another atom of bromine. On adding the theoretical quantity of bromine to the cold acetic acid solution of the bromacenaphthalide,

white tufts of needle-shaped crystals separate out, consisting of the respective dibromacenaphthalides.

α_4 -Brom- β_2 -amido- β'_2 , or β'_2 -Bromonaphthalene; m. p. 105° .

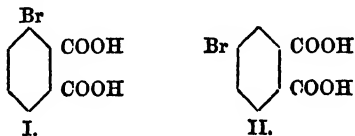
The brominated acetyl-derivative of α_4 -brom- β_2 -naphthylamine, when purified by crystallisation from alcohol, forms white needles melting at 221 — 222° . Some of the substance was boiled for about eight hours with strong alkali; the acetyl-group was removed by the end of this time, and the dibromonaphthylamine floated as a dark oily layer on the surface. When cool this oil solidified, and after being washed free from alkali was crystallised repeatedly from dilute alcohol with the addition of animal charcoal till white silky needles were obtained having a fusing point of 105° . The substance is not basic, and is readily soluble in alcohol, ether, benzene, acetone, &c.

0.1748 gram burnt with lime gave 0.2180 gram AgBr.

Theory for $C_{10}H_6Br_2 \cdot NH_2$.	Found.
Br 53.15	53.07

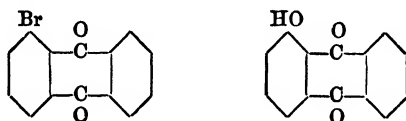
In order to determine the constitution of this dibromonaphthylamine, some of the pure substance was oxidised by repeated evaporation on a water-bath with dilute nitric acid. The residue was found to contain a bromophthalic acid, of which the anhydride sublimed in white needles fusing at 134 — 135° . The acid itself when crystallised from water had a melting point of 174° , and appears, therefore, to be identical with the acid obtained by Guareschi by the oxidation of his nitrobromonaphthalene (m. p. 122.5°), and of which the anhydride was found to fuse at 131 — 132° . In the present dibromonaphthylamine, one bromine-atom is, therefore, in each benzene-ring, and it only remains to determine the position taken up by the second atom, that of the NH_2 -group and the first bromine-atom being known.

Only two bromophthalic acids are theoretically possible, viz. :—



By heating phthalic acid with bromine and water at 180 — 200° , Faust obtained (*Annalen*, 160, 62) a bromophthalic acid melting at 138 — 140° , of which the anhydride, according to H. v. Pechmann (*Ber.*, 12, 2126), melts at 60 — 65° ; he further states that the direct bromination of phthalic acid furnishes two isomeric bromophthalic acids, the chief product being Faust's modification. The other modi-

fication formed was not isolated in a state of purity. The mixed bromophthalic acids dissolved in benzene and warmed with aluminium chloride gave, as the chief product, a bromobenzoylbenzoic acid, $C_6H_5Br \cdot \begin{matrix} COOH.....(1) \\ CO \cdot C_6H_5... (2) \end{matrix}$, which, when heated with strong sulphuric acid, passed into bromanthraquinone, the latter on fusion with alkali furnishing Graebe and Liebermann's erythroxyanthraquinone (*Annalen*, 160, 141; 183, 151; *Ber.*, 4, 109, and 5, 868). The bromo- and oxyanthraquinones thus obtained are accordingly regarded by H. v. Pechmann as ortho-compounds:—

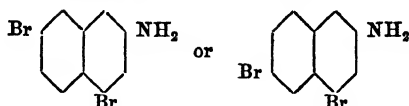


The bromophthalic acid melting at 138—140° would, on this view, have the formula I.

Another bromophthalic acid, of which the anhydride was stated to fuse at 125°, was obtained by A. J. Smith (this Journal, 35, Trans., 792) by the oxidation of tetrabromo- β -naphthol; the melting point of this acid was not given by the author. Guareschi (*loc. cit.*), as already stated, obtained a bromophthalic acid melting at 174—176° (anhydride at 131—132°) by oxidising his nitrobromonaphthalene (m. p. 122·5°), and, notwithstanding the difference of melting point, he regards this acid as identical with Smith's, and isomeric with Faust's and H. v. Pechmann's modification.

In view of the fact that only two bromophthalic acids are theoretically possible, it appeared to me to be desirable to clear up this discrepancy between the statements of Smith and Guareschi with respect to the melting points of their respective bromophthalic anhydrides, the more especially as my own product had a melting point 9—10° higher than that given by Smith. Of the purity of my own specimen, I satisfied myself by repeatedly subliming it from hot sand till the melting point was perfectly constant. A quantity of tetrabromo- β -naphthol was accordingly prepared by brominating β -naphthol in glacial acetic acid, and, after purification, this was oxidised in an alkaline solution of potassium permanganate in the usual way. When pure, the bromophthalic acid thus obtained had a melting point of 174°, and the anhydride fused at 133—135°, so that there can be no doubt as to the identity of Smith and Guareschi's acids.

From these results, it follows that if formula I be assigned to Faust's acid, the constitution of the present dibromonaphthylamine must be—



It will be shown subsequently that the evidence is at present insufficient to decide conclusively between these alternative formulæ.

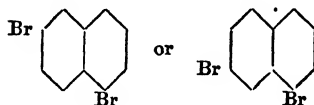
$\alpha_1\beta'_2$ -, or $\alpha_1\beta'_3$ -Dibromonaphthalene; m. p. 74° .

The foregoing dibromonaphthylamine was dissolved in strong sulphuric acid, the solution diluted with a small quantity of water, sodium nitrite added, and the diazo-sulphate decomposed by absolute alcohol in the usual way. The displacement of the NH_2 -group furnished a dibromonaphthalene, which, after one or two crystallisations from dilute alcohol using animal charcoal, was obtained in the form of flat glistening needles; these when dry presented the appearance of lustrous silvery scales having a melting point of 74° .

0.2324 gram burnt with lime gave 0.3043 gram AgBr.

	Theory for $\text{C}_{10}\text{H}_6\text{Br}_2$.	Found.
Br	55.94 per cent.	55.72

In its crystalline form and general appearance, this dibromonaphthalene is perfectly distinct from any of the modifications with which I am acquainted. It is possibly identical with that melting at $76-77^\circ$, which Darmstädter and Wichelhaus (*Ann. Chem. Pharm.*, **152**, 298) obtained by brominating $\alpha\text{-C}_{10}\text{H}_7\text{SO}_3\text{H}$, but I have not yet seen a specimen of this modification, and am not, therefore, at present able to decide this point. The constitution may be thus expressed:—



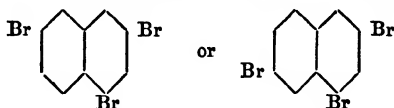
$\beta_2\alpha_1\beta'_2$ -, or $\beta_2\alpha_1\beta'_3$ -Tribromonaphthalene; m. p. 110° .

The dibromonaphthylamine last described was diazotised and converted into diazo-perbromide, and the latter decomposed by warming with glacial acetic acid. The resulting tribromonaphthalene, after several crystallisations from alcohol, formed short white needles melting at 110° , and resembling in its general properties the modification (m. p. $113-114^\circ$) formerly described (this Journal, **43**, 1883, Trans., 4), from which it is, however, quite distinct in constitution.

0.1225 gram burnt with lime gave 0.1890 gram AgBr.

Theory for $C_{10}H_6Br_3$.		Found.
Br	65.75 per cent.	65.66

The constitution of this compound may be thus expressed:—



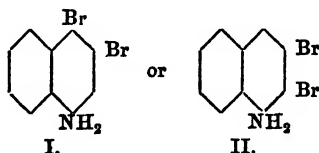
β_2 -Brom- α_4 -amido- α'_1 , or α'_4 -Bromonaphthalene; m. p. 101—102°.

The acetyl-derivative of β_2 -brom- α_4 -naphthylamine was dissolved in glacial acetic acid, and brominated as in the case of the preceding modification. White stellate clusters of the dibromacenaphthalide soon separated, and after crystallisation from alcohol had a melting point of 221°. After hydrolysis by boiling with strong caustic soda, the dibromonaphthylamine was obtained by crystallisation from dilute alcohol in the form of white needles melting at 101—102°.

0.2040 gram burnt with lime gave 0.2554 gram AgBr.

Theory for $C_{10}H_5Br_2NH_2$.		Found.
Br	53.15 per cent.	53.27

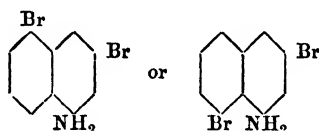
In most of its properties, this modification resembles the dibromonaphthylamine previously described, but is rather more basic, dissolving in boiling dilute acids, and being precipitated from the solution by alkalis. When repeatedly evaporated to dryness with dilute nitric acid, it left a resinous residue from which a minute quantity of a crystalline substance sublimed on gently heating, and at the same time a much larger quantity of some oily product distilled off; this did not solidify on cooling. The crystalline portion proved to be a trace of phthalic anhydride, but this was far too small in quantity to warrant the supposition that the second bromine-atom had entered the same benzene nucleus with the other substituents. Were this the case, the formula of this dibromonaphthylamine would be—



On displacing the NH_2 -group by hydrogen a compound of formula I would furnish orthodibromonaphthalene (m. p. 63°; this Journal, 43, 1883, Trans., 5), while a compound of formula II might be

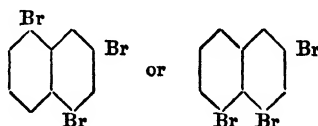
expected to give the hitherto unknown $\beta_2\text{-}\beta_3$ -dibromonaphthalene. In order to decide this experimentally some of the dibromonaphthylamine was diazotised, and treated in the usual way with absolute alcohol. The resulting dibromonaphthalene, after purification by several crystallisations from alcohol, appeared to be identical in every respect with the $\alpha_1\text{-}\beta'_2$, or $\alpha_1\text{-}\beta'_3$ -modification (m. p. 74°) described above. From this it follows that neither of the foregoing formulæ is correct, and that the second bromine-atom, therefore, in this case also enters the unsubstituted nucleus, probably in an α' position.

Although I have not succeeded in isolating Faust's bromophthalic acid from the oxidation products of the present dibromonaphthylamine, as might have been expected on the view last put forward, it is certain that Smith and Guareschi's acid is not present, as this forms a well characterised anhydride. The oily substance above referred to as being obtained from these oxidation products was found to contain bromine, and it is possible that it consists of a mixture of Faust's acid (anhydride) with some oily impurity. Unfortunately, the quantity was too small to enable me to attempt any purification, but even with the results obtained the evidence points with sufficient distinctness to the conclusion that this dibromonaphthylamine has one of the following formulæ:—



$\beta_2\text{-}\alpha_1\text{-}\alpha'_1$ -, or $\beta_2\text{-}\alpha_1\text{-}\alpha'_4$ -Tribromonaphthalene; m. p. 105° .

The preceding dibromonaphthylamine was diazotised and converted into diazo-perbromide, the latter, which formed an orange crystalline substance, being decomposed by warming with glacial acetic acid in the usual way. After purification, the resulting tribromonaphthalene is scarcely distinguishable in appearance and general properties from the tribromonaphthalene previously described, but its melting point is lower, and I have little doubt as to its being a distinct modification. In accordance with the results previously obtained, the constitutional formula may be—



Theoretical Considerations.

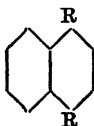
It has already been stated that the evidence at present available does not render it possible to decide between the alternative formulæ given to the present dibromonaphthylamines and their derived di- and tri-bromonaphthalenes. The facts which have to be expressed are that both dibromonaphthylamines give rise to the same dibromonaphthalene and to different tribromonaphthalenes. The difficulty in question arises from the circumstance that these facts can be equally well explained by two hypotheses. This is shown in the accompanying formulæ (p. 517), which are arranged in developmental series, and which, at the same time, serve to summarise the results so far obtained.

Looked at from the general point of view that in the naphthalene derivatives the tendency of the substituents is to occupy symmetrically opposite positions, the formulæ required by the first hypothesis are perhaps the more probable.

One fact brought out very clearly by the present investigation is that compounds which are undoubtedly isomeric may be undistinguishable by their melting points and general appearance, so that great caution is necessary before deciding on such grounds as to the identity of two substances. Thus, in the foregoing series of formulæ it is seen that the nitrobromonaphthalenes, bromacenaphthalides, and dibromacenaphthalides in each of the two series have practically the same melting points, and it is only when the derivatives of these compounds are studied that the isomerism which is known to exist reveals itself.













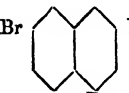
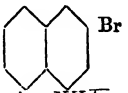
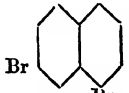
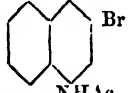
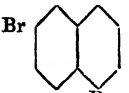
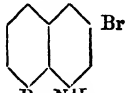
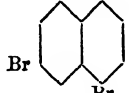
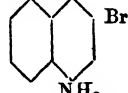
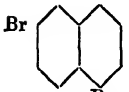
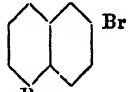
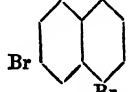
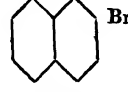
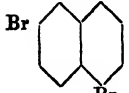
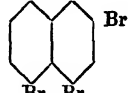
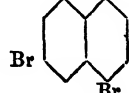

Another point which will be observed is that throughout the series the effect exerted by the position of the NH_2 -group is most marked; those compounds in which this group occupies an α -position invariably melt at a lower temperature, and have more decidedly basic characters than those in which this group occupies a β -position. It may be said in other words that the individuality of α - and β -naphthylamine extends throughout their di- and tri-bromo-derivatives.

As a general result of this and previous researches, it appears that in para-derivatives of naphthalene the law of substitution very closely follows that governing the substitution in the benzene series. Thus, in compounds of the general formula—

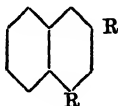


the first product of substitution at low temperatures appears to be a

compound of the formula $\alpha_1\beta_2\alpha_1$, the analogy to the benzene series being most marked when $\alpha_1R = NH\bar{A}c$, and the substituent is NO_2 or a halogen-atom. In striking contrast with this, it appears from the

First hypothesis.		Second hypothesis.	
			
M. p. 131-132°.	M. p. 131°.	M. p. 131-132°.	M. p. 131°.
			
M. p. 71·5°.	M. p. 62°.	M. p. 71·5°.	M. p. 62°.
			
M. p. 186·5°.	M. p. 187°.	M. p. 186·5°.	M. p. 187°.
			
M. p. 221-222°.	M. p. 221°.	M. p. 221-222°.	M. p. 221°.
			
M. p. 105°.	M. p. 101-102°.	M. p. 105°.	M. p. 101-102°.
			
M. p. 74°.	M. p. 74°.	M. p. 74°.	M. p. 74°.
			
M. p. 110°.	M. p. 105°.	M. p. 110°.	M. p. 106°.

results made known in the present paper that in meta-derivatives of the general formula—



a new law comes into action, which causes the substituent to enter the opposite ring, the position taken up by this substituent being determined by the relative positions of β_2R and α_1R with respect to one another.

I may take the present opportunity of pointing out that in mono-derivatives of naphthalene the law of substitution also follows in most cases that which obtains in the benzene series. Thus α -derivatives generally give rise to para-derivatives of the formula $\alpha_1\text{--}\alpha_1$, as we see when α -acenaphthalide is brominated or nitrated, when α -naphthylamine and α -naphthol are sulphonated, and when α -bromonaphthalene is nitrated. Even the supposed anomalous behaviour of the β -mono-derivatives is not altogether abnormal when considered in the light of analogy with the benzene series. Thus in the latter series, in cases where para-derivatives would ordinarily result from substitution in a mono-derivative, ortho-derivatives are generally produced if the *para*-position is not open. Now in β -mono-derivatives of naphthalene the *para*-position with respect to the β -substituent is not open, and the second substituent in such cases generally enters the *ortho*- α -position, as we see when β -naphthol is brominated or sulphonated at a low temperature, when β -naphthol is converted into a nitroso-derivative, or when β -acenaphthalide is brominated or nitrated.

V. IODINE DERIVATIVES OF NAPHTHALENE.

The only iodine-derivatives of naphthalene at present known are α -iodonaphthalene, a heavy oily liquid boiling above 300° , obtained by the action of iodine on mercury dinaphthyl (Otto and Moeries, *Annalen*, **167**, 1868, 164),* and β -iodonaphthalene (P. Jacobson, *Ber.*, **14**, 804), a white crystalline substance (m. p. $54\cdot5^\circ$) obtained by the diazo-reaction from β -naphthylamine. It seemed desirable to take advantage of the materials accumulated and the experience gained in the course of the preceding investigations in order to extend our knowledge of the naphthalene series to the hitherto unknown di- and tri-derivatives containing iodine. The experiments have in the first

* This modification can also be readily prepared from α -naphthylamine by decomposing the diazo-sulphate with hydriodic acid.

place been mainly directed towards the preparation of the diiodo-naphthalenes.

Nitroiodonaphthalenes.

Preliminary experiments having shown that neither α - nor β -acenaphthalide could be directly iodated, the mixed nitracenaphthalides obtained by the nitration of α -acenaphthalide in acetic acid were saponified by the action of alcoholic potash and the nitronaphthylamines, after being collected, washed, and dried, were dissolved in dilute sulphuric acid, and the well-cooled solution diazotised by the addition of the theoretical quantity of sodium nitrite. The solution of the diazo-sulphate was decomposed in the usual way by hydriodic acid. Nitrogen was given off with brisk effervescence, and the reaction was completed on standing for a few hours at the ordinary temperature. The dark ochreous precipitate was collected, washed, and crystallised from alcohol with the addition of animal charcoal. The solution on cooling deposited microscopic whitish needles of nitroiodonaphthalene, and the mother-liquor on standing for some days gave a crystalline deposit consisting of a second modification.

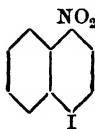
α_1 -Nitro- α_1 -iodonaphthalene; m. p. 123° . The first crystals deposited, which constitute the chief product, were obtained pure after two or three crystallisations from alcohol, and then had a constant melting point of 123° .

0.2462 gram burnt with lime gave 0.1950 gram AgI.

Theory for $C_{10}H_6I \cdot NO_2$.
42.47 per cent. I.

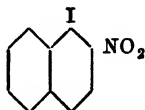
Found.
42.81

The substance is soluble in benzene, acetic acid, acetone, &c. When treated with powerful reducing agents the iodine is removed and α -naphthylamine regenerated, so that the constitution is—



β_2 -Nitro- α_1 -iodonaphthalene; m. p. 108.5° . The crystals which had separated from the mother-liquor after the removal of the preceding modification were crystallised from alcohol till the melting point was constant. Beautiful yellow scales were thus obtained, which fused at 108.5° . The nitro-group in this modification cannot be reduced by any means without the simultaneous removal of the iodine-atom, β -naphthylamine (m. p. 112°) being the result of the reduction.

This nitroiodonaphthalene is accordingly derived from the orthonitronaphthylamine, and its constitutional formula is—



In order to analyse this compound advantage was taken of the ease with which the iodine is removed by reducing agents. The alcoholic solution was treated with zinc-dust and dilute sulphuric acid, the solution neutralised with sodium carbonate, and the precipitate of zinc carbonate and excess of zinc filtered off, well washed with water, and the filtrate evaporated to dryness and ignited till free from β -naphthylamine. The residue was dissolved in water, the solution filtered, acidified with nitric acid, and precipitated by silver nitrate in the usual way. This method of analysis was rendered necessary on account of the great stability of the nitroiodonaphthalene, which required passing over a very long column of red-hot lime to insure complete decomposition. The great excess of lime thus required rendered the ordinary process of analysis extremely inconvenient, and the analytical results were very unsatisfactory till this method of reduction was adopted.

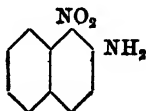
0.2239 gram gave 0.1758 gram AgI.

Theory for $C_{10}H_6I \cdot NO_2$.
42.47 per cent. I

Found.
42.43

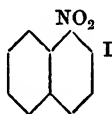
α -Nitro- β -iodonaphthalene; m. p. 88.5° . A third nitronaphthalene has been obtained from α -nitro- β -acenaphthalene (P. Jacobson, *Ber.*, 14, 805) by the substitution of iodine for NH_2 in the corresponding nitronaphthylamine. In order to saponify the nitracenaphthalide, which was prepared by the nitration of β -acenaphthalide in glacial acetic acid according to Jacobson's method, the substance was mixed with a small quantity of water and sulphuric acid added until complete solution was effected. The flask was then gently heated on a water-bath for about an hour, and the contents afterwards mixed with water. The orange precipitate of nitronaphthylamine was collected, washed, and crystallised from dilute alcohol.

This nitronaphthylamine is the fourth known modification, and has not hitherto been described. It forms orange needles melting at $123-124^\circ$. Its constitution is—



It possesses no basic characters, and is but slightly soluble in boiling water; it dissolves readily in alcohol, acetone, and acetic acid. No platinochloride could be obtained by the addition of PtCl_4 to the alcoholic solution in the presence of hydrochloric acid; the orange crystals which separated from the solution consisted of unaltered nitronaphthylamine. The solutions of the substance have considerable tinctorial power, dyeing silk and wool of a fine yellow colour.

In order to convert the foregoing nitronaphthylamine into nitroiodonaphthalene, the solution of the diazo-sulphate was decomposed by hydriodic acid in the usual way. The crude ochreous substance resulting from the reaction was purified by several crystallisations from alcohol, and was finally obtained in the form of pale straw-coloured glistening needles, melting at 88.5° , and resembling the preceding modification in its behaviour towards solvents. From the constitution of the nitronaphthylamine from which it is derived the formula of this compound is—



Diiodonaphthalenes.

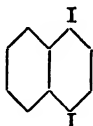
These compounds were obtained by reducing the nitroiodonaphthalenes, diazotising the resulting iodonaphthylamines, and decomposing the diazo-salts with hydriodic acid. Only two modifications have as yet been obtained.

$\alpha_1\text{-}\alpha_2$ -*Diiodonaphthalene*; m. p. $109\text{--}110^\circ$. On dissolving α -nitro- α -iodonaphthalene in glacial acetic acid, and agitating the cold solution with zinc-dust, reduction takes place without the removal of the iodine-atom. The iodonaphthylamine which remains in the solution is very unstable, rapidly oxidising to a red colouring matter on exposure to the air. The free base has not, therefore, as yet been isolated. The sulphate $(\text{C}_{10}\text{H}_7\text{I}\cdot\text{NH}_2)_2\text{SO}_4$, separates out in the form of white needles on adding dilute sulphuric acid to the acetic acid solution; this salt appears to be tolerably stable.

The most advantageous method of dealing with the unstable solution of iodonaphthylamine was found to be the following:—After filtering off the excess of zinc-dust as rapidly as possible, dilute sulphuric acid was immediately added to the diluted solution, and the theoretical quantity of sodium nitrite dissolved in water at once run in. The solution of the diazo-sulphate, which is quite stable, was filtered to remove a small quantity of some tarry impurity, and hydriodic acid added to the filtrate in the usual way. The brown

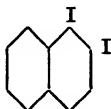
precipitate resulting from the foregoing reaction was crystallised repeatedly from alcohol with the addition of animal charcoal, and the whitish needles thus obtained finally had a constant melting point of 109–110°.

This diiodonaphthalene corresponds to the dichloronaphthalene of m. p. 67–68°, and to the dibromonaphthalene of m. p. 81°, and closely resembles the latter in its general properties. The constitutional formula is—



$\alpha_1\beta_2$ -Diiodonaphthalene; m. p. 81°. Owing to the fact already mentioned that β -nitro- α -iodonaphthalene could not be reduced without the removal of the iodine-atom, this modification could not be employed for the preparation of the orthodiiodonaphthalene. A preliminary experiment with α -nitro- β -iodonaphthalene showed however that the nitro-group could be reduced in this modification without the removal of the iodine-atom; the resulting iodonaphthylamine appeared, moreover, to be more stable than the para-modification, but unfortunately the quantity of material at my disposal was too small to enable me to attempt the isolation of the free base.

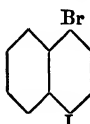
The reduction of α -nitro- β -iodonaphthalene was effected by means of zinc-dust in the cold acetic acid solution, and the necessary quantity of sodium nitrite solution was at once run into the filtrate from which the excess of zinc-dust had been filtered, and which had been strongly acidified with dilute sulphuric acid. The brown precipitate resulting from the decomposition of the diazo-sulphate by hydriodic acid was purified by successive crystallisations from alcohol with animal charcoal, and the substance was at length obtained in the form of white scaly crystals melting sharply at 81°. This modification corresponds to the orthodibromonaphthalene (m. p. 63°), and has the constitution expressed by the formula—



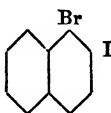
I have not as yet succeeded in obtaining metadiiodonaphthalene for want of material, although this modification could most probably be prepared by nitrating paraiodacenaphthalide, saponifying, displacing the NH_2 -group by hydrogen, reducing the metanitroiodonaphthalene, and then replacing the NH_2 -group by iodine by the diazo-reaction.

Bromiodonaphthalenes.

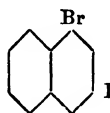
The three following modifications have been obtained :—



I.



II.



III.

- I. *α_1 -Bromo- α_4 -iodonaphthalene.* Prepared by diazotising parabromo- α -naphthylamine (m. p. 94°) and decomposing the diazo-sulphate by hydriodic acid. Long flat colourless needles; m. p. 83.5° .
- II. *α_1 -Bromo- β_2 -iodonaphthalene.* Prepared by decomposing the diazo-sulphate of Cosiner's bromonaphthylamine (m. p. 63° ; *Ber.* 14, 59) with hydriodic acid. Opaque thick white needles; m. p. 94° .
- III. *α_1 -Bromo- β_2 -iodonaphthalene.* Prepared by decomposing the diazo-sulphate of the α -brom- β -naphthylamine (m. p. 71.5°), described in the previous part of this paper, with hydriodic acid. Long whitish needles; m. p. 68° .

These bromiodonaphthalenes are all very similar in general properties, being insoluble in water and soluble in alcohol, acetone, and glacial acetic acid, and extremely soluble in the benzene hydrocarbons, and ether. The modification Br:I = β_2 - α_1 , analogous to III in the above formulæ, has not been prepared owing to want of material.

α_4 -Iod- α_1 -acenaphthalide; m. p. 196° .

The corresponding nitroiodonaphthalene (m. p. 123°) was dissolved in glacial acetic acid, and the cold solution agitated with zinc-dust; the resulting iodonaphthylamine was at once acetylated by adding acetic anhydride to the filtered solution and boiling for about 15 minutes. The iodacenaphthalide was precipitated by water, collected, washed till free from acid, and purified by several crystallisations from alcohol. The pure substance formed white needles having the melting point above given, and resembling the corresponding parabromacenaphthalide in its general properties.

α_4 -Iodo- β_2 -nitro- α_1 -acenaphthalide; m. p. about 235 — 236° .

In order to prepare this substance it was found most advantageous to heat a strong acetic acid solution of the foregoing iodacenaphthalide with about twice the theoretical quantity of nitric acid (1.42 sp. gr.)

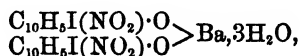
to a temperature of 70—80° for one or two hours. The nitro-compound partly separates from the solution, when cold, in the form of ochreous needles, and a further quantity is precipitated from the mother-liquor on the addition of water. After crystallisation from alcohol, the substance was obtained in the form of straw-coloured needles, melting apparently at about 235—236°, but at the same time subliming to a considerable extent, and thus rendering the determination of the exact melting point very difficult. This nitroiodacenaphthalide could not be saponified by the action of sulphuric acid with the same facility as the nitrobromacenaphthalides; the substance appears to undergo partial decomposition with the liberation of iodine when acted on by the acid, and want of material has prevented experiments with other saponifying agents.

α₁-Iodo-β₁-nitro-α₁-naphthol; m. p. 145—146°.

The foregoing idonitracenaphthalide is readily decomposed on boiling it with strong caustic alkalis, ammonia being given off and idonitronaphthol formed. The latter was obtained by acidifying the alkaline solution, and after crystallisation from alcohol formed yellow needles having the above melting point. The potassium and sodium derivatives separate from their solutions as orange microscopic needles, soluble in cold and more readily soluble in hot water. The barium salt was obtained by adding a solution of barium chloride to a solution of the sodium salt; it forms a bright red amorphous powder, almost insoluble in boiling water. The quantity of salt obtained was only sufficient for a barium estimation.

0.2310 gram gave 0.0652 gram BaSO₄ = 16.59 per cent. Ba.

This corresponds with the formula—



which requires 16.72 per cent. Ba. This salt is analogous, therefore, to that of the bromonitronaphthol previously described. The dry salt deflagrates somewhat suddenly when ignited.

A determination of iodine in the free idonitronaphthol gave the following results:—

0.2592 gram burnt with lime gave 0.1927 gram AgI.

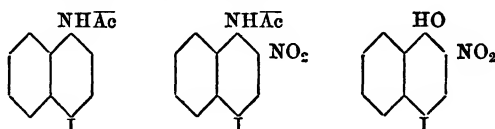
Theory for C₁₀H₅I(NO₂)·OH.
40.31 per cent. I.

Found.
40.18

This idonitronaphthol is insoluble in cold water, and only imparts a slight yellow colour to boiling water; it dissolves sparingly in hot

benzene and more readily in alcohol, acetic acid, and acetone. It acts as a brilliant yellow dye when silk or wool is immersed in a solution of one of the alkaline salts which has been previously acidified.

The constitution of the foregoing compounds is doubtless analogous to that of the corresponding bromine-derivatives :—



This view is confirmed by the fact that idonitronaphthol, when oxidised either by nitric acid or by potassium permanganate in alkaline solution, gives a large quantity of phthalic acid.

α_1 -Iodo- β_2 -naphthol; m. p. 94.5° .

As no iodine-derivative of the naphthols has hitherto been obtained, experiments were undertaken with the object of preparing some of these compounds, and in a former paper (this Journal, **39**, Trans., 47) I briefly called attention to the discovery of a new iodine-derivative of β -naphthol, concerning which I am now able to give some further particulars.

It will be of interest in the first place to describe the method of preparation, more especially as the method of iodising in question, which may be of general application, offers advantages over the older methods, which necessitated the employment of iodic acid or mercuric oxide.

20 grams of pure β -naphthol, 20 grams of lead acetate, and about the same weight of powdered anhydrous sodium acetate, are all dissolved by the aid of heat in an excess of glacial acetic acid. As soon as all the ingredients have dissolved, the clear solution is cooled and 35.2 grams of iodine, dissolved in hot acetic acid, are gradually added to the first solution, which is agitated after each addition of iodine. The latter is rapidly absorbed and a heavy yellow precipitate of lead iodide separates; this precipitate is filtered off and the filtrate diluted with water, when a white flocculent mass, consisting of microscopic needles, separates. The crude product is collected on a filter, washed thoroughly with cold water, and purified by crystallisation from dilute alcohol or acetic acid. This purification is best effected by dissolving the substance in an excess of the warm solvent and gradually diluting with warm water till the milkiness caused by the latter disappears only with some difficulty. On cooling, tufts of colourless prismatic needles separate out, and after repeating the process the substance is quite pure and fuses constantly at 94.5° .

In order to determine the iodine, advantage was taken of the property possessed by the compound of giving up its halogen on reduction. A weighed quantity (dried in a vacuum over sulphuric acid) was dissolved in alcohol, and treated with zinc-dust and dilute sulphuric acid. The solution was then diluted with water, excess of sodium carbonate added, and the zinc compounds separated by filtration. The filtrate, together with the washings, was evaporated to dryness and ignited till all organic matter had been destroyed. The residue was dissolved in water, filtered, acidified with dilute nitric acid, and the iodine precipitated by silver nitrate.

0.2963 gram gave 0.2565 gram AgI.

Theory for $C_{10}H_6I \cdot HO$.
47.03 per cent. I.

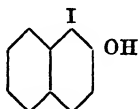
Found.
46.78

Iodo- β -naphthol is slightly soluble in boiling water, separating on cooling in the form of long filamentous needles. It dissolves also in acetic acid, alcohol, acetone, ether, the benzene hydrocarbons, and petroleum. The crystals which separate from the latter solvent are especially large and well formed. The substance is soluble in cold dilute solutions of caustic alkalis, the small and finely divided crystals dissolving instantaneously and the larger crystals with less readiness. If the alkaline solution is strong, or if heat is applied before the whole of the substance has dissolved, decomposition takes place with formation of some insoluble compound which has not yet been examined. The production of this compound, which in many cases still retained the crystalline form of the original substance, at first led me to form the erroneous conclusion that the iodine compound was itself insoluble in alkalis, and that substitution had taken place in the hydroxylic hydrogen with production of β -naphthyl-oxyiodide, $C_{10}H_7OI$.*

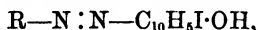
Iodo- β -naphthol gradually darkens on keeping, a specimen prepared about a year ago being now almost black, although kept in a dark place. By the action of nitric acid, either alone or when added to the acetic acid solution of the substance, the whole of the iodine is liberated, and some nitro-derivative of β -naphthol is formed, but this has not yet been further examined. The iodine is also readily removed, as already stated, by nascent hydrogen, reduction taking place either in an acid or alkaline solution and β -naphthol being produced. When heated in a dry tube decomposition takes place with the

* In order to see whether such a compound could be formed under conditions most favourable to its production, some β -naphthol was iodised by the method described, the solutions being kept well cooled throughout the whole operation. The product was, however, soluble in dilute caustic alkaline solutions, and identical in all respects with that previously obtained.

liberation of iodine vapour. By oxidation with potassium permanganate in an alkaline solution a large quantity of phthalic acid was obtained. The compound is thus doubtless analogous to the monobromo- β -naphthol obtained by A. J. Smith (this Journal, **35**, Trans., 782), and its constitutional formula may be written:—



When heated with dimethylaniline, iodo- β -naphthol gives methyl-violet, and with aniline, after heating for some time, a red colouring matter is formed and β -naphthol regenerated. It may be of interest to add that acetyl- β -naphthol, $C_{10}H_7 \cdot O \cdot C_2H_3O$, cannot be iodised by the method which so readily gives iodo- β -naphthol. Iodo- β -naphthol readily enters into combination with diazo-compounds, forming a series of colouring matters of the general formula



where R stands for any benzene or naphthalene residue, sulphonated or otherwise.

By the foregoing method of iodising, α -naphthol is apparently converted into dinaphthol, but as the specimen employed contained β -naphthol, the further examination of the product must be for the present postponed.

These researches have been conducted in the laboratory of Messrs. Brooke, Simpson, and Spiller, at the Atlas Works, Hackney Wick, and I have great pleasure in again expressing my thanks to this firm for the opportunities which they have afforded me of carrying on these investigations.

LIX.—*On the Non-crystallisable Products of the Action of Diastase upon Starch.*

By HORACE T. BROWN and G. H. MORRIS, Ph.D.

THERE is perhaps no one subject in the whole range of chemistry which has attracted more workers during the last sixty years than the transformations which starch undergoes when submitted to the action of diastase or dilute acids; and on no subject are the opinions of chemists, even at the present time, more at variance.

With regard to the nature of the *crystallisable* portion of the pro-

ducts, there is now, mainly owing to the work of O'Sullivan, but little difference of opinion, but the properties and constitution of the *uncrystallisable* products, the so-called *dextrins*, are still open to controversy, no two chemists who have made a special study of the subject entirely agreeing in their interpretation of the results. This is mainly owing to the great difficulty in obtaining the dextrins in anything like a pure state, to the alteration and separation which they undergo during purification, and, lastly, to the very few known processes to which, when isolated, they can be submitted, in order to determine their properties and their points of resemblance or difference.

The present communication may be looked upon as a continuation of a paper on starch and its transformations, read before this Society by one of us a few years ago (Brown and Heron, this Journal, Trans., 1879, 596). More extended work now enables us to add certain facts tending towards a more accurate knowledge than we have hitherto possessed of the molecular changes involved in the splitting-up of starch.

In order the better to appreciate the extent of the wide divergence of opinion as to the nature of the dextrins, and the present state of our knowledge of them, it will be necessary to refer, somewhat in detail, to their history.

The earliest notice we have been able to discover of the production of a gummy matter from starch by the action of acid was in 1812, by Vogel (*Schweigg. Jour.*, 5, 80), but in the previous year Vauquelin (*Bull. de Pharm.*, 3, 54) had observed that starch, when strongly heated, is wholly converted into a body resembling gum-arabic. A body of the same nature was found by De Saussure in 1819 (*Ann. Chim. Phys.*, 11, 379) amongst the products of decomposition of starch-paste left to itself.

The gum produced from starch by the limited action of dilute acid, first received a careful examination in 1833, at the hands of Biot and Persoz (*Ann. Chim. Phys.*, 52, 72), who, from its strong power of rotating a ray of plane polarised light to the right gave to it the name of *dextrin*. From the description given of the dextrin, its rotatory power cannot have exceeded $[\alpha]_D^{174}$, and it must have been far from homogeneous. Biot and Persoz consider that it is not a product of the decomposition of the starch, but agree with Raspail (*Ann. des Sciences Naturelles*, 6, 334) that it consists of the contents of the starch granules, freed from their outer coating by the action of the acid.

The first notice of a dextrin prepared from starch by *diastase* was in 1833 by Payen and Persoz (*Ann. Chim. Phys.*, 53, 73), who

describe it as a body soluble in cold water and in weak alcohol, and not coloured by iodine. In 1836, Payen (*Ann. Chim. Phys.*, **61**, 355) stated that the rotatory power of his dextrin was equal to that of starch, and that it had an elementary composition indicated by the formula $C_6H_{10}O_5$. He further considered that the dextrins produced by dilute sulphuric acid, diastase, and torrefaction respectively, are mere physical modifications of the same substance; but this idea was strongly opposed by Mulder some years afterwards (*Chemie des Bieres*, 1858, 166).

Up to the year 1860, dextrin was considered as occupying a position intermediate between starch and sugar, that in fact, by the action of acid or diastase, starch was converted first into dextrin, and the dextrin, by subsequent hydration, into sugar. In the above-mentioned year, Musculus (*Compt. rend.*, **50**, 785) brought forward a certain amount of evidence to show that dextrin and sugar are not *successively* formed products, but are produced *simultaneously* by a splitting-up of the starch molecule. The evidence adduced by Musculus in his earlier papers in support of this view is far from being conclusive, and his interpretation of the results is vitiated by the error he fell into, in common with nearly all other chemists, of considering the sugar to be dextrose. Nevertheless, this theory has led to much good work, and there is now plenty of evidence that, in a more extended form, it is capable of including most of the known facts.

The dextrin described more in detail by Musculus in 1865 (*Ann. Chim. Phys.* [4], **6**, 177) was a body not coloured by iodine, and was without reducing action on Fehling's solution. It was also said not to be attacked by diastase, but this was strenuously denied by Payen (*Ann. Chim. Phys.* [4], **4**, 286), who contended that diastase saccharifies it most easily. The reason for the difference of opinion on this point will be evident later on.

It now began to be recognised amongst chemists that there are at least *two* dextrins derivable from starch, the one coloured red or brown by iodine, and the other giving no coloration with that reagent. These were described by Griessmayer in 1871, as Dextrin I and Dextrin II (*Annalen*, **160**, 40), and a year later O'Sullivan distinguished them as α - and β -dextrin. These are, perhaps, better known as erythrodextrin and achroodextrin, names first proposed by Brücke in 1872 (*Wien. Acad. Ber.* [3], **65**, 126), as indicative of their behaviour with iodine.

O'Sullivan in 1872 (this Journal, **25**, 579), submitted these dextrins, prepared both by diastase and dilute acid, to a careful examination. He concluded that they both have the same specific rotatory power $[\alpha]_D^{213^\circ}$, and an elementary composition indicated by the formula

$C_6H_{10}O_5$. He never succeeded in obtaining them quite free from cupric oxide reducing power, but brings forward good evidence to prove that they would not possess this property could they be obtained in a state of complete purity. Both the α - and β -dextrins are slowly converted into maltose by the action of malt-extract.

In 1875, Bondonneau, apparently entirely unaware of the previous work of O'Sullivan, describes (*Compt. rend.*, 81, 972, 1210) these dextrins, which he denotes by α , β , and γ respectively. His α -dextrin, which is identical with the α -dextrin of O'Sullivan and the erythro-dextrin of Brücke, is said by Bondonneau to have a specific rotatory power of $[\alpha]186^\circ$, whilst his β -dextrin, which appears to be an achroodextrin, and similar to the substance described by O'Sullivan under the same name, has a specific rotatory power of $[\alpha]176^\circ$. After the precipitation of these two dextrins with alcohol from the products of the starch transformation, the solution, according to Bondonneau, contains glucose, and from 24.6 to 29.8 per cent. of a non-reducing body, which he names γ -dextrin, and which he considers to have a specific rotatory power of $[\alpha]_D164^\circ$. He states that both α - and β -dextrins are attacked by diastase, but the former much more readily than the latter. In 1876, O'Sullivan (this Journal, 1876, i, 479), in an important paper on maltose, contended that Bondonneau's γ -dextrin has no existence, but is only the difference between the reducing powers of maltose and dextrose, the latter having been erroneously considered by Bondonneau as the sugar of starch transformations. This objection is, we have no doubt, in the main well founded, but from the absence of details in Bondonneau's paper, and from a confusion between $[\alpha]$, and $[\alpha]_D$, in noting the specific rotatory powers, it is impossible to re-cast the results in an intelligible form. There can be no question, however, that Bondonneau's experiments do not prove the existence of a third dextrin.

Amongst the derivatives of starch insoluble in alcohol, there had hitherto been recognised with certainty but two dextrins, characterised by their different behaviour with iodine. It was not until the year 1878, that it began to be suspected that the body passive to iodine, which had been variously described as achroodextrin by Brücke, as β -dextrin by O'Sullivan, and as Dextrin II by Griessmayer, was in reality a mixture of several dextrins. This suggestion was first made by Musculus and Gruber (*Bull. Soc. Chim.*, 30, 54), who, by the action of diastase on starch under varying conditions of temperature, prepared three so-called achroodextrins, which they state have the following optical and reducing properties:—

Achroodextrin	I.	$[\alpha]210^\circ$	Reducing power,	12.
"	II.	$[\alpha]199^\circ$	"	" 12.
"	III.	$[\alpha]190^\circ$	"	" 12.

When these dextrins were isolated, and were acted on with fresh diastase, their properties were modified as follows:—

Achroodextrin	I.	$[\alpha]159^\circ$.	Reducing power,	36.
„	II.	$[\alpha]168^\circ$.	„	20.
„	III.	Unchanged.		

Musculus and Gruber look upon the Achroodextrin II as a mixture of I and III, which they denote in the latter part of their paper as Achroodextrins α and β respectively.

By the continued action of diastase in the cold on the transformation-products primarily obtained at $50-60^\circ$, they consider that a third body is produced with $[\alpha]150^\circ$ and $\kappa 28$, which they have named Achroodextrin γ .

Although there can be no doubt, from certain considerations to which we shall refer later on, that these dextrins of Musculus and Gruber, and also the products of their further transformation, cannot have been pure, yet the remarkable differential action of diastase on them certainly to some extent justifies the authors in their assertion that the achroodextrins from starch are not identical, and that under the action of diastase they produce so much the more sugar the less the starch from which they have been derived has been saccharified.

It was in this same paper that Musculus and Gruber first advanced a definite theory of the gradual breaking down of the starch molecule by a series of hydrations and successive decompositions; maltose being formed at each splitting-up of the starch molecule, together with a dextrin of less molecular weight. In a paper read before the Society by one of us and Heron in 1879 (Trans., 1879, 596), it was stated that we had also arrived at a similar explanation of the hydrolysis of starch, whilst approaching the subject from a different direction. We stated our conviction that the dextrins are not meta-meric, but polymeric bodies, those corresponding to transformations of high optical activity being of greater molecular complexity than those derived from transformations of lower optical activity.

We considered that soluble starch could not have a simpler formula than $10C_{12}H_{20}O_{10}$, and that, under the action of malt-extract, groups of $C_{12}H_{20}O_{10}$ were successively removed by hydrolysis in the form of maltose, the residue in each case being a dextrin, whose molecule became of course less complex as the groups of $C_{12}H_{20}O_{10}$ were removed.

On this hypothesis, which is essentially identical with that of Musculus and Gruber, the number of distinct dextrins must depend on the molecular weight of the lowest possible dextrin in the series. From a careful consideration of all the facts we brought forward, it

seems most probable that the lowest dextrin, due to actual hydrolysis, is formed when the transformation-products have reached a position of the greatest stability indicated by an optical activity of $[\alpha]_{D^{20}} 162.6$, and a reducing power of $\kappa_{3.86} 49.3$. If this is the case, there are eight possible dextrins derivable from the $10C_{12}H_{20}O_{10}$ molecule of starch, the dextrin of lowest molecular weight being slowly converted into maltose by simple hydration. For further proof of the existence of these dextrins, we must refer to the original paper (*loc. cit.*)

Almost simultaneously with the appearance of the last-mentioned paper, O'Sullivan submitted to the Society (Trans., 1879, 770), a criticism of the above-mentioned work of Musculus and Gruber, accompanied by a statement of his more recent views on the constitution of the dextrins. In this paper, he abandons his original idea of the identity of the achroodextrins, and considers the existence of *four* distinct dextrins as highly probable. These are the dextrins of his A, B, and C equations, with the addition of another derived from his B' equation.*

We have thus, according to O'Sullivan's latest views—

(1) α -Dextrin, coloured brownish-red by iodine, and produced when starch breaks up according to his C equation.

Dextrins not coloured by iodine—

(2) β -Dextrin I = the dextrin of his B equation.

(3) β -Dextrin II = the dextrin of his B' equation.

(4) β -Dextrin III = the dextrin of his A equation.

These dextrins were isolated, in a more or less pure state, by precipitation with alcohol, and it was found that the nearer they approached purity, the less power they possessed of reducing cupric oxide. It is concluded that in a pure state they would all be free from reducing power, and that they would all have the same optical activity, viz., $[\alpha]_D 222^\circ$.†

If the view be correct that the starch molecule, being broken

* This B' equation corresponds exactly with Brown and Heron's Transformation 5, giving $[\alpha]_{D^{20}} 182.1$, and $\kappa_{3.86} 31.3$, and yielding maltose equal to 51.3 per cent. of the total products.

† Throughout this paper by O'Sullivan the values representing $[\alpha]$, and κ are based upon *actual weighed quantities* of the substance under analysis, and not as hitherto upon quantities deduced from the sp. gr. of solutions. This must be carefully borne in mind when comparing the values with those previously given by O'Sullivan, and by Brown and Heron, which are based upon a divisor for the sp. gr. of 3.85 and 3.86 respectively. Since these divisors are undoubtedly too low for dextrin by about 3 per cent., the values of $[\alpha]$, and κ given by O'Sullivan in this paper must be reduced by that amount in order to render such a comparison possible.

down by hydrolysis, yields first maltose and α -dextrin, this latter body breaking down into maltose and β -dextrin, which in turn splits up into maltose and β -dextrin II, and so on, maltose and a dextrin of lower molecular weight being produced at each step; then O'Sullivan considers that when the dextrans so produced are put under certain conditions of temperature, comparable with those under which his various equations hold good with starch, they ought to behave as follows: the α -dextrin ought to yield *three* definite proportions of maltose; β -dextrin I at least *two*; β -dextrin II should yield at least *one*; whilst β -dextrin III should yield no absolutely definite proportion.

When this was tested by actual experiment, under the necessary conditions of temperature, the probable results indicated above were not obtained, the dextrans, when isolated, appearing to behave differently with malt-extract from the same dextrans when in solution with the products formed simultaneously with them. It was found also that some of the dextrans, β -dextrin I and β -dextrin II for example, which undoubtedly were formed by reactions expressed by different equations, were acted on to the same extent when isolated. Taking these facts into consideration, and also that "when an action takes place with starch, or any of these dextrans, the whole of the body in solution is affected at the same time," O'Sullivan concludes that the production of maltose from starch and the dextrans is not due to the breaking down of the molecule; and that, as far as the dextrans are concerned, we have not to do with a series of polymerides, "but rather a series of bodies of the same molecular weight, in which differences in their behaviour to the agent under consideration, must be accounted for by a difference in *relation in the arrangement* of the molecules to one another, probably in solution only." An attempt is then made to give an idea of what this arrangement may be, but as the wording of this part of the paper is somewhat obscure, we must confess our inability to gain a clear idea of the author's meaning, or a definite conception of the points of difference between his new hypothesis and the older one, involving a gradual degradation of the dextrin molecule.

In 1879, we had also a further contribution to this difficult subject from Herzfeld ("Ueber Maltodextrin," Halle, 1879, also *Ber.*, 12, 2120), who regards the transformation of starch by diastase not as a splitting-up of the molecule, but as giving rise consecutively to amyloextrin (soluble starch), erythroextrin, and achroodextrin, the last-mentioned substance being converted into *maltodextrin* and maltose.

When starch is transformed at temperatures below 65°, maltose and Brücke's achroodextrin are formed, the latter, when purified, having

no reducing action on Fehling's solution. At temperatures above 65°, there are produced only erythrodextrin and a body soluble in dilute alcohol but insoluble in alcohol of 90 per cent., which Herzfeld has named *maltodextrin*.

Maltodextrin is said to have an optical activity of $[\alpha]_D^{171.6^\circ}$, and a reducing power of 23.5. Unlike erythro- and achroo-dextrin, it is as readily soluble in cold water as ammonium acetate, and it is only slightly more soluble in hot than in cold water. Herzfeld looks upon

it as two dextrin-groups united to a sugar-group, thus: $\left\{ \begin{array}{l} \text{C}_6\text{H}_{10}\text{O}_5 \\ \text{C}_6\text{H}_{10}\text{O}_5 \\ \text{C}_6\text{H}_{12}\text{O}_6 \end{array} \right.$ It

is said to be completely fermentable by yeast.

From the results of the analysis of this body, and from the fact that considerable quantities of malt-extract were used in its preparation, there can be no doubt that the maltodextrin, as described by Herzfeld, must have been very impure; but we shall show later on in this paper that a body, which may be looked upon as a combination of maltose and dextrin, does most probably exist in starch transformations carried on under certain conditions, but that its optical and reducing properties are not those ascribed to it by Herzfeld, and that it does not occupy the position in the series of starch products which has been assigned to it.

Sufficient has now been stated in the above *résumé* of the more important work on the dextrins to indicate the very different views which are even now entertained of their nature and origin.

That we have, during the last decade, advanced somewhat in our knowledge of these bodies there can be no doubt, this advance being mainly due to the comparatively recent recognition of several distinct dextrins not coloured by iodine; and to the pretty general acceptance of the theory of molecular degradation of the starch, which was first published by Musculus and Gruber. An acceptance of this theory removes many difficulties and reconciles many apparently antagonistic statements, more especially those relating to the action of diastase on dextrin. That Musculus and Gruber have ascribed wrong properties to their dextrins there can be but little doubt, but that the theory of the successive breaking down of the starch molecule into maltose and a series of polymeric dextrins is, in the main, a correct expression of the facts, and the only theory at present brought forward which is capable of wholly containing those facts, we consider equally beyond question.

It has been shown in a previous paper by one of us (Brown and Heron, *Trans.*, 1879, 596) that when starch-paste is acted on by malt-extract at any temperature above 40°, the specific rotatory

power and cupric oxide reducing power of the products both agree in indicating the existence of maltose ($[\alpha]_{D^{20}} 150, \kappa_{D^{20}} 61$)*, and a non-reducing dextrin with a specific rotatory power of $[\alpha]_{D^{20}} 216^\circ$. When all the precautions we have described, as necessary for correcting for the malt-extract, are rigorously carried out, the results are singularly concordant, and quite confirm the previous statements of O'Sullivan on this point.

The same holds good for the various precipitates obtained by fractionally precipitating the transformation-products with alcohol; the composition of all the fractions is capable of interpretation on the supposition that they consist of maltose and a non-reducing dextrin. This is indicated by the following experiments:—

A transformation of starch was made at 62° , the quantity of malt-extract employed (0.5 c.c. per 5 grams starch) being limited in order to reduce to a minimum its disturbing effects in the subsequent operations. The reaction was arrested at the end of an hour, when we found for the starch-products (corrected)—

$$\begin{array}{r} [\alpha]_{D^{20}} 204.3^\circ \\ \kappa_{D^{20}} 10.5 \end{array}$$

From this we deduce the composition—

$$\begin{array}{rcl} \text{Maltose..} & 17.2 & \\ \text{Dextrin..} & 82.8 & \\ \hline & 100.0 & \end{array} \left. \vphantom{\begin{array}{r} 17.2 \\ 82.8 \\ 100.0 \end{array}} \right\} \begin{array}{l} \text{requiring } [\alpha]_{D^{20}} 204.6^\circ \\ \kappa_{D^{20}} 10.5 \end{array}$$

After evaporation to a syrup, we proceeded to fractionate this mixture with alcohol in the following manner:—The thick syrup was heated to 100° , and alcohol of 90 per cent. was gradually poured in until a slight permanent precipitate was produced, the whole being kept heated on the water-bath. The liquid was then put on one side to cool, when the clear solution was poured off from the substance which had separated out. This clear liquid was then treated on the water-bath with more alcohol, until a permanent precipitate was again produced. The process was repeated five times, and we thus obtained five different fractions of the original substance, and a final mother-liquor. Each fraction was dissolved in water, reprecipitated once more with strong alcohol, taken up with water, again evaporated, and dried in a vacuum.

The analysis of each fraction is given below, and also the composition calculated from the reducing power and the specific rotatory

* For an exact definition of these symbols, we must refer to the above-mentioned paper (Trans., 1879, 596).

power, corresponding to this composition, for comparison with the observed specific rotatory power.

$$\begin{array}{rcl}
 \text{Fraction I.} & [\alpha]_{j3.86} 207.0^\circ & \\
 & \kappa_{3.86} 10.1 & \\
 \text{Maltose..} & 16.5 & \\
 \text{Dextrin..} & 83.5 & \left. \begin{array}{l} \text{requiring } [\alpha]_{j3.86} 205.0^\circ \\ \kappa_{3.86} 10.1 \end{array} \right\} \\
 \hline
 & 100.0 &
 \end{array}$$

$$\begin{array}{rcl}
 \text{Fraction II.} & [\alpha]_{j3.86} 206.2^\circ & \\
 & \kappa_{3.86} 5.6 & \\
 \text{Maltose..} & 9.1 & \\
 \text{Dextrin..} & 90.9 & \left. \begin{array}{l} \text{requiring } [\alpha]_{j3.86} 209.9^\circ \\ \kappa_{3.86} 5.6 \end{array} \right\} \\
 \hline
 & 100.0 &
 \end{array}$$

$$\begin{array}{rcl}
 \text{Fraction III.} & [\alpha]_{j3.86} 203.8^\circ & \\
 & \kappa_{3.86} 8.3 & \\
 \text{Maltose..} & 13.6 & \\
 \text{Dextrin..} & 86.4 & \left. \begin{array}{l} \text{requiring } [\alpha]_{j3.86} 207.0^\circ \\ \kappa_{3.86} 8.3 \end{array} \right\} \\
 \hline
 & 100.0 &
 \end{array}$$

$$\begin{array}{rcl}
 \text{Fraction IV.} & [\alpha]_{j3.86} 201.5^\circ & \\
 & \kappa_{3.86} 13.6 & \\
 \text{Maltose..} & 22.3 & \\
 \text{Dextrin..} & 77.7 & \left. \begin{array}{l} \text{requiring } [\alpha]_{j3.86} 201.2^\circ \\ \kappa_{3.86} 13.6. \end{array} \right\} \\
 \hline
 & 100.0 &
 \end{array}$$

$$\begin{array}{rcl}
 \text{Fraction V.} & [\alpha]_{j3.86} 200.3^\circ & \\
 & \kappa_{3.86} 17.1 & \\
 \text{Maltose..} & 28.0 & \\
 \text{Dextrin..} & 72.0 & \left. \begin{array}{l} \text{requiring } [\alpha]_{j3.86} 197.5^\circ \\ \kappa_{3.86} 17.1 \end{array} \right\} \\
 \hline
 & 100.0 &
 \end{array}$$

There was now left the strongly alcoholic filtrate from Fraction V. This contained only a small quantity of matter in solution, which was contaminated with the whole of the malt-extract bodies soluble in alcohol, and which must in this case have amounted to about 5 per cent. of the starch-products remaining in solution in the last filtrate. Analysis gave—

$$\begin{array}{rcl}
 & [\alpha]_{j3.86} 167.5^\circ & \\
 & \kappa_{3.86} 35.4 &
 \end{array}$$

corresponding to the composition of—

Maltose.....	58.0	} requiring $[\alpha]_{j3.86} 167.5^\circ$ $\kappa_{j3.86} 35.4$
Dextrin.....	37.2	
Inactive malt-extract bodies	4.8	
	<hr/> 100.0	

Another similar experiment was made by fractionating the products of a transformation in which the starch had been more fully converted. The numbers for the starch-products (corrected) were—

$$\begin{array}{l} [\alpha]_{j3.86} 196.4^\circ \\ \kappa_{j3.86} 18.6 \end{array}$$

from which the following composition was deduced:—

Maltose..	30.4	} requiring $[\alpha]_{j3.86} 195.9^\circ$ $\kappa_{j3.86} 18.6$
Dextrin..	69.6	
	<hr/> 100.0	

In fractionally precipitating this product, a careful note was taken of the exact strength of the alcoholic liquids (percentage by volume), from which the precipitates were separated. The small quantity of substance which came down from 38 per cent. alcohol, consisting principally of malt-extract bodies, was rejected.

Fraction I. From 48.3 per cent. alcohol.

$$\begin{array}{l} [\alpha]_{j3.86} 209.3^\circ \\ \kappa_{j3.86} 5.49 \end{array}$$

Maltose..	9.0	} requiring $[\alpha]_{j3.86} 210.0^\circ$ $\kappa_{j3.86} 5.49$
Dextrin..	91.0	
	<hr/> 100.0	

Fraction II. From 59.4 per cent. alcohol.

$$\begin{array}{l} [\alpha]_{j3.86} 209.6^\circ \\ \kappa_{j3.86} 8.85 \end{array}$$

Maltose..	14.5	} requiring $[\alpha]_{j3.86} 206.3^\circ$ $\kappa_{j3.86} 8.85$
Dextrin..	85.5	
	<hr/> 100.0	

Fraction III. From 67 per cent. alcohol.

$$\begin{array}{l} [\alpha]_{j3.86} 203.1^\circ \\ \kappa_{j3.86} 9.0 \end{array}$$

$$\left. \begin{array}{r} \text{Maltose.. } 14\cdot7 \\ \text{Dextrin.. } 85\cdot3 \\ \hline 100\cdot0 \end{array} \right\} \text{requiring } [\alpha]_{j3\cdot86} 206\cdot2^{\circ} \\ \kappa_{3\cdot86} \quad 9\cdot0$$

Fraction IV. From 74 per cent. alcohol.

$$\begin{array}{r} [\alpha]_{j3\cdot86} 202\cdot4^{\circ} \\ \kappa_{3\cdot86} \quad 13\cdot18 \\ \text{Maltose.. } 21\cdot6 \\ \text{Dextrin.. } 78\cdot4 \\ \hline 100\cdot0 \end{array} \left\} \text{requiring } [\alpha]_{j3\cdot86} 201\cdot3^{\circ} \right. \\ \kappa_{3\cdot86} \quad 13\cdot18$$

Fraction V. From 81·5 per cent. alcohol.

$$\begin{array}{r} [\alpha]_{j3\cdot86} 199\cdot09^{\circ} \\ \kappa_{3\cdot86} \quad 14\cdot53 \\ \text{Maltose.. } 23\cdot8 \\ \text{Dextrin.. } 76\cdot2 \\ \hline 100\cdot0 \end{array} \left\} \text{requiring } [\alpha]_{j3\cdot86} 200\cdot2^{\circ} \right. \\ \kappa_{3\cdot86} \quad 14\cdot53$$

The *filtrate* from this last fractional precipitation contained 60·40 grams of solids, which had a specific rotatory power of $[\alpha]_{j3\cdot86} 175\cdot5^{\circ}$, and a reducing power of $\kappa_{3\cdot86} 31\cdot5^{\circ}$. There is in this case a correction requisite for the solids of the 66 c.c. of malt-extract which had been originally used in the transformation, and of which 77 per cent. was soluble in alcohol of 81·5 per cent. A measured portion of the malt-extract was treated with alcohol of this strength, and a determination made of the amount of substance left in solution with its optical rotation and reducing power. On applying the correction to the filtrate from Fraction 5, the starch-products gave—

$$\begin{array}{r} [\alpha]_{j3\cdot86} 185\cdot6^{\circ} \\ \kappa_{3\cdot86} \quad 29\cdot4 \\ \text{Maltose.. } 48\cdot1 \\ \text{Dextrin.. } 51\cdot9 \\ \hline 100\cdot0 \end{array} \left\} \text{requiring } [\alpha]_{j3\cdot86} 184\cdot1^{\circ} \right. \\ \kappa_{3\cdot86} \quad 29\cdot4$$

We could quote, if more proof were required, many other experiments of a similar nature, all tending in the same direction. Just as the total products of starch transformations brought about by malt-extract always yield numbers indicating the existence only of maltose and a non-reducing dextrin, so it is equally beyond question that the same holds good with regard to any portion of those products which

can be separated by fractionation with alcohol. We have thus, we consider, established a criterion of purity for the products of the action of diastase on starch. In those cases in which the observations of other writers do not conform with the above rule, we have no hesitation in ascribing the discrepancy either to the presence of impurities or to errors in analysis.*

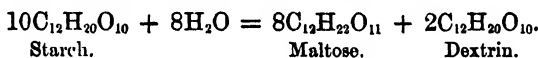
The tendency of all transformations carried on with malt-extract between 40° and 60° is speedily to attain a point of equilibrium beyond which further progress is relatively very slow. This point of equilibrium is reached when the mixed products possess the following properties :—

$$\begin{array}{l} [\alpha]_{j3.86} 162.6^{\circ} \\ \kappa_{3.86} 49.3 \end{array}$$

This corresponds with a composition of—

Maltose..	80.9
Dextrin..	19.1
	<hr/>
	100.0

and to the reaction represented by the equation—



All transformations of starch which yield a higher rotatory power than 162.6°, and a lower reducing power than 49.3°, are speedily brought to this point by treatment with a little fresh malt-extract at 50°. Since maltose is not acted on by this treatment, the cause of change must be looked for in the degradation of the dextrin, and it became a matter of great importance to ascertain if the dextrin would behave in a similar manner and be affected to the same extent when isolated; for if this should be the case, it ought to be possible to ascertain the position which any dextrin may occupy in the polymeric series by determining the amount of degradation it undergoes with malt-extract at 50—60°.

As a preliminary to the experiments bearing on this point, it was necessary to ascertain first of all, whether the dextrans during the ordinary processes of separation and purification undergo any hydrolysis. In order to settle this, the following *quantitative* experiments were made :—

* These remarks apply to experiments in which the transformation and the subsequent digestion have been completed within a few hours. When digestion with the active agent is continued for several days, a little *dextrose* is no doubt produced, as stated by Musculus and Gruber, and of course under these conditions the rule mentioned above ceases to hold good.

A transformation of starch-paste having been made with malt-extract previously heated to 66° , the products were evaporated to a thin syrup, after having been treated with a little alcohol to partially free them from malt-extract bodies. The syrup on analysis showed :—

$$\begin{array}{r} [\alpha]_{j3.96} 188.1^{\circ} \\ \kappa_{3.96} 20.2 \end{array}$$

A known quantity of this, containing 203 grams of solid matter, was digested with boiling alcohol for a considerable time. The clear liquid was poured off, the residue taken up with boiling water, evaporated, and treated again with boiling alcohol. This process was repeated *eight* times in succession. All the clear alcoholic filtrates were added together, the alcohol distilled off, and the residue made up to a definite volume and analysed. The dextrin left after the eight successive treatments was evaporated with water to drive off alcohol, and also made up with water to a definite volume. During all these processes the greatest care was taken to avoid all loss of substance, but no especial precaution was taken with regard to the conditions of precipitation and evaporation, these being carried on exactly in the same manner as is customary during the preparation and purification of the dextrins.

Now it is evident that if no hydrolysis of the dextrin has taken place during this treatment, the values of $[\alpha]_D$ and κ of the separate portions, soluble and insoluble in alcohol, ought, when recombined, to give mean results in accordance with those afforded by the transformation-products *before* treatment.

The portion of the transformation-product, dissolved by the alcohol, amounted to 107.91 grams, or 53.15 per cent.; whilst the residual dextrin amounted to 95.14 grams, or 46.85 per cent. of the original substance. The following are the results obtained :—

	Per cent.	$[\alpha]_{j3.96}$	$\kappa_{3.96}$
Portion insoluble in alcohol....	46.85	206.5°	8.52
„ soluble in alcohol.....	53.15	178.8°	31.50
	100.00	—	—
Calculated mean	—	191.7°	20.7
Original starch-products	—	188.1°	20.2

Hence the processes described above have been carried on without materially altering the composition of the starch-products.

The last experiment was conducted with starch-products containing only the *achroodextrins*; it seemed, therefore, desirable to repeat it with an *erythro*dextrin, which, from its higher position in the series and its consequent greater molecular complexity, might be more readily broken down by the processes employed.

A partially purified dextrin of this nature was prepared, and submitted to a treatment similar to the last, the experiment being again made *quantitatively*. After *five* separate precipitations with alcohol, with the necessary re-solution and evaporation, 24 per cent. of the substance was found to be dissolved by the alcohol, having a cupric oxide reducing power of $\kappa_{3.86}21.8$, whilst the residue amounted to 76 per cent. with a reducing power of $\kappa_{3.86}3.6$. The calculated mean is $\kappa_{3.86}7.96$ against $\kappa_{3.86}7.9$ for the original substance, so that here again no hydrolysis has taken place.

We may conclude, therefore, that fractional precipitation with alcohol, and a moderate amount of heating with water and evaporation, do not break up the molecules of the higher dextrins to any appreciable extent, a change which is so readily effected by a mere trace of malt-extract.

We are now in a better position to examine the action of malt-extract on the separated dextrins, and to compare this with its action on the same dextrins when in solution with the products of transformation produced simultaneously with them. The principal point to be ascertained may be put definitely as follows. On fractionating the products of a starch-transformation with alcohol, is the mean maximum hydrolysing effect of malt-extract, acting separately on the portions soluble and insoluble in alcohol, the same as the maximum hydrolytic action exercised under similar conditions on the original transformation-products?

Some of the products of a starch-transformation at 66° were partially purified from malt-extract bodies, after which they gave on analysis—

$$[\alpha]_{D^{66}}188.1^{\circ}$$

$$\kappa_{3.86}20.2$$

A solution containing about 5.5 grams per 100 c.c. was acted on with malt-extract (10 c.c. extract to 5.5 grams of substance) at 55° , and gave the following results, the action in the samples taken for analysis being arrested by means of salicylic acid as previously described:—

	$[\alpha]_{D^{55}}$	$\kappa_{3.86}$
Original solution	188.1°	20.2
After 1 minute	169.3	—
„ 2½ minutes	164.6	—
„ 10 „	164.0	—
„ 20 „	163.4	—
„ 30 „	159.3	43.2
„ 60 „	159.3	—

* The point of maximum conversion, corresponding to our No. 8 transformation, was reached in 30 minutes; the results are, like those of the original liquid, slightly lower than is required by theory, owing to the presence of about 3 per cent. of malt-extract bodies, which, however, are of no consequence in these particular experiments.

The original transformation-products were now separated by *eight distinct treatments* with alcohol, and the soluble and insoluble portions *separately* treated with malt-extract at 55° as before.

A. Portion soluble in alcohol:—

	$[\alpha]_{53.86^\circ}$	$\kappa_{53.86^\circ}$
Before action of malt-extract	178.8°	31.5
After 1 minute	156.1	—
„ 5 minutes	151.4	—
„ 10 „	148.0	—
„ 30 „	146.8	57.4
„ 60 „	146.8	—

B. Portion insoluble in alcohol:—

	$[\alpha]_{53.86^\circ}$	$\kappa_{53.86^\circ}$
Before action of malt-extract	206.5°	8.5
After 1 minute	192.1	—
„ 5 minutes	190.5	—
„ 10 „	189.4	—
„ 20 „	186.7	—
„ 30 „	186.7	26.4
„ 60 „	186.7	—

Since the original products were made up of 53.1 per cent. of A, and 46.8 per cent. of B, we get the following numbers as a measure of the final action of the malt-extract:—

	$[\alpha]_{53.86^\circ}$	$\kappa_{53.86^\circ}$
1. Mean result of the action of malt-extract on the fractions separately.....	160.6°	42.8
2. Result of the action of malt-extract on the original starch-products	159.3	43.2

In another similar experiment, the mean result of the action of malt-extract on the fractions separately showed a fall of angle to 162.2°, whilst the original transformation was reduced to 164.3°. In this case, there was not quite such a close correspondence in the values of κ , the numbers coming out 40.7 for the fractions, and 44.4 for the original solution.

Since the action of malt-extract at 50—60° on the mixed products of transformation always brings the dextrin down to a given point, and

the total action is not altered by previously separating the starch-products by alcohol, it follows that we here ought to have a valuable means of differentiating the dextrins, of testing their homogeneity, and of ascertaining the position they occupy in the polymeric series. This ought to be possible even when they are wholly or partially separated by alcohol, fermentation or otherwise, from the remaining portion of the starch-products which were split off *pari passu* with them.

In the following table, we have given the theoretical quantity of maltose which 100 parts of the dextrins corresponding to each of the transformations would yield, if degraded to the No. 8 dextrin, which is the one corresponding to the stable equation yielding $[\alpha]_{D-86} 162.6^\circ$, $\kappa_{D-86} 49.3$.

No. of transformation.	Constants of mixed products.		Maltose yielded by 100 parts of each dextrin when degraded to No. 8.
	$[\alpha]_{D-86}$	κ_{D-86}	
Soluble starch. .	216.0°	—	84.44
1 ..	209.0	6.4	82.09
2 ..	202.2	12.7	79.20
3 ..	195.4	18.9	75.39
4 ..	188.7	25.2	70.37
5 ..	182.1	31.3	63.33
6 ..	175.6	37.3	52.77
7 ..	169.0	43.3	35.18
8 ..	162.6	49.3	00.00

If we have a dextrin under examination, and ascertain the maximum amount of maltose which it will yield by *hydrolysis* with malt-extract at 50—60°, we can by means of this table fix its position in the series, and determine the particular reaction which has given rise to it. If we are dealing with a mixture of dextrins we can of course in this way only determine their *mean* position.

We shall now be able to examine more in detail the dextrins derived from the various transformations.

From transformations corresponding to No. 8 of the series, we can only separate one dextrin which is incapable of being further *hydrolysed* by malt-extract at 50—60°, but which is very slowly *hydrated* to maltose.

With transformations higher in the series than No. 8, the case is different, for in these we can always find indications, more or less strongly marked, that the dextrin is not homogeneous. In other words, from such transformations we can always, by fractionating with alcohol, obtain dextrins which are proved not to be identical by the fact that they yield, on maximum hydrolysis, different quantities

of maltose. This holds good even in those cases in which we have had reason to believe that saccharification of the starch corresponds exactly with any particular equation.

As a proof of these statements, we may instance the following examples of numerous similar experiments:—

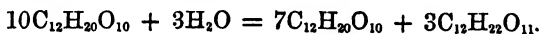
A starch conversion was made with malt-extract, previously heated to 66°, using 5 c.c. of extract for 5 grams of starch. After conversion, the corrected results of the analysis were:—

$$\begin{array}{r} [\alpha]_{j3.86} 193.8^\circ \\ \kappa_{3.86} \quad 22.0 \end{array}$$

This corresponds to—

$$\begin{array}{rcl} \text{Maltose.} & 36.0 & \\ \text{Dextrin.} & 64.0 & \\ \hline & 100.0 & \end{array} \left. \vphantom{\begin{array}{r} 36.0 \\ 64.0 \\ 100.0 \end{array}} \right\} \text{requiring } \begin{array}{r} [\alpha]_{j3.86} 192.2^\circ \\ \kappa_{3.86} \quad 22.0 \end{array}$$

The transformation is very nearly that of No. 3, and this is further indicated by the degradation of the products with malt-extract at 60°, by which 100 parts of the dextrin gave on hydrolysis 74.0 parts of maltose, the exact theoretical quantity being 75.3. So far we should certainly have a right to consider that the starch has been broken down according to the equation—



That this equation must represent the *mean* transformation there can be no doubt, but it is quite possible that the starch has split up partly according to higher and partly according to lower equations. The solution of the problem is in all probability to be found in the examination of the fractionated dextrins; for it is almost certain that all the dextrins have not the same solubility in alcohol; so that if the transformation has proceeded according to a single equation the fractionated dextrins will be identical, whereas if it has proceeded according to several equations the precipitated dextrins will indicate this by their different behaviour with malt-extract. In order to test this, the above starch-conversion was evaporated to a syrup, treated with a little alcohol to partially free it from malt-extract bodies, and then precipitated with alcohol.

Residue 1 gave—

$$\begin{array}{r} [\alpha]_{j3.86} 196.8^\circ \\ \kappa_{3.86} \quad 15.0 \end{array}$$

corresponding to—

Maltose..	24.5	} which requires $[\alpha]_{D^{+86}} 199.8^{\circ}$ $\kappa_{D^{+86}} 15.0$
Dextrin..	75.5	
	<hr/> 100.0	

On treating a definite quantity of this with malt-extract at 60°, the dextrin which it contained, when fully hydrolysed, yielded 64.6 per cent. of its weight of maltose, and hence corresponded nearly with the dextrin No. 5 of our series.

The above residue was then treated repeatedly with boiling alcohol which left behind—

Residue 2, which on analysis gave—

$$\begin{array}{l} [\alpha]_{D^{+86}} 195.0^{\circ} \\ \kappa_{D^{+86}} 18.9 \end{array}$$

corresponding to a composition of—

Maltose..	30.9	} which requires $[\alpha]_{D^{+86}} 195.0^{\circ}$ $\kappa_{D^{+86}} 18.9$
Dextrin..	69.1	
	<hr/> 100.0	

This dextrin-residue on hydrolysis with malt-extract at 60°, yielded an additional amount of maltose equal to 60 per cent. of the dextrin it contained. The dextrin corresponded to that of a theoretical transformation intermediate between Nos. 5 and 6.

Residue 3, which was obtained from residue 1 by further repeated treatment with alcohol, gave—

$$\begin{array}{l} [\alpha]_{D^{+86}} 200.9 \\ \kappa_{D^{+86}} 6.9 \end{array}$$

This dextrin, which had been much reduced in quantity by the frequent treatment with alcohol, contained about 3 per cent. of the malt-extract bodies. Its properties correspond to a composition of—

Maltose.....	11.3	} which requires $[\alpha]_{D^{+86}} 200.9^{\circ}$ $\kappa_{D^{+86}} 6.9$
Dextrin.....	85.1	
Inactive malt-extractives	3.6	
	<hr/> 100.0	

On degradation with malt-extract at 60°, the dextrin contained in this fraction yielded only 35.5 per cent. of maltose, so that its position in the series was almost exactly that of No. 7 transformation.

These results, taken in conjunction with those given earlier in the paper, indicate that the dextrin of the original transformation, although apparently that of No. 3, could not have been homogeneous,

for whilst it gave on complete hydrolysis 74 per cent. of maltose, we have been able to separate from it dextrans yielding respectively 64.6, 60.0, and 30 per cent., the complement of these necessary to make up the original mixed dextrans, having been removed in the alcoholic filtrates, as will be shown further on in describing somewhat similar experiments.

The results of another experiment with an erythro-dextrin may be given briefly as follows. In this case the mixed products of transformation, when corrected, gave—

$$\begin{array}{r} [\alpha]_{j3.86} 204.3 \\ \kappa_{3.86} 10.5 \end{array}$$

corresponding to a composition of—

$$\left. \begin{array}{r} \text{Maltose.. } 17.2 \\ \text{Dextrin.. } 82.8 \\ \hline 100.0 \end{array} \right\} \text{which requires } \begin{array}{r} [\alpha]_{j3.86} 204.6 \\ \kappa_{3.86} 10.5 \end{array}$$

The dextrin of this, on degradation with malt-extract at 60°, yielded 77.1 per cent. of maltose, so that its apparent position in the Transformation Series is nearly that of No. 2, the dextrin of which yields 79.2 per cent.

The separation of the dextrans was carried on in a different manner from that of the previous experiment, the starch-products being submitted to a system of fractionation. Into the evaporated syrup kept hot was poured alcohol of 90 per cent., until a permanent precipitate was formed. When cold, the liquid was poured off the precipitate, which we call Fraction I, and after heating was again treated with hot alcohol in the same manner, Fractions III, IV, and V being successively separated as the liquid became richer in alcohol. Each of the various fractions was degraded with malt-extract at 60° to the lowest limit of hydrolysis. The following numbers represent the amount of maltose yielded by 100 parts of the dextrin of each fraction:—

I	63.3	per cent. maltose.
II	65.3	" "
III	74.4	" "
IV	86.5	" "
V	89.7	" "
Mean	75.4	Original dextrans, 77.1.

Here, again, the dextrin of a transformation, which, from its preparation and analysis, we should have good reason to believe was repre-

sented by a definite equation (No. 2 of our series, or O'Sullivan's C equation), has been shown not to be homogeneous but mixed.

We will give the details of one more experiment of even a more accurate nature than the foregoing, and one in which all the precautions suggested by long experience in such work had been taken. Besides proving the proposition immediately under consideration, viz., that the apparently homogeneous transformations are in reality not so, this experiment also affords additional evidence of the truth of the preceding propositions, viz. (1), that nothing can be separated out from the products of a starch-transformation with malt-extract, which will not analyse out as maltose and a non-reducing dextrin; and (2) that the mean action of malt-extract on the separated fractions of a transformation is equal to its action on the original products.

The transformation of starch was in this case made with a little "diastase," freshly prepared from a very active malt-extract, by the process recommended by O'Sullivan (Trans., 1884, 2). The action was arrested when iodine gave the maximum coloration for erythro-dextrin. Analysis then showed—

$$\begin{array}{l} [\alpha]_{j3.86} 202.2^{\circ} \\ \kappa_{3.86} 12.4, \end{array}$$

corresponding to a composition of—

$$\begin{array}{rcl} \text{Maltose..} & 20.3 & \\ \text{Dextrin..} & 79.7 & \\ \hline & 100.0 & \end{array} \left. \vphantom{\begin{array}{r} 20.3 \\ 79.7 \\ 100.0 \end{array}} \right\} \text{which requires } \begin{array}{l} [\alpha]_{j3.86} 202.5^{\circ} \\ \kappa_{3.86} 12.4 \end{array}$$

On degradation of this transformation with malt-extract at 60°, it attained the maximum limit of hydrolysis in a few minutes, when analysis gave—

$$\begin{array}{l} [\alpha]_{j3.86} 163.5^{\circ} \\ \kappa_{3.86} 49.9 \end{array}$$

$$\begin{array}{rcl} \text{Maltose..} & 81.8 & \\ \text{Dextrin..} & 18.2 & \\ \hline & 100.0 & \end{array} \left. \vphantom{\begin{array}{r} 81.8 \\ 18.2 \\ 100.0 \end{array}} \right\} \text{requires } \begin{array}{l} [\alpha]_{j3.86} 162.0^{\circ} \\ \kappa_{3.86} 49.9 \end{array}$$

In acquiring this composition, which corresponds almost theoretically with Transformation 8, the dextrin has yielded 75 per cent. of maltose on degradation.

A known quantity of the liquid was then evaporated to a thin syrup, and fractionated with alcohol of gradually increasing strength, in the same way as in the last experiment.

The following figures give the strength of the alcohol from which each fraction was precipitated, and the weight of each fraction expressed as a percentage of the total amount.

Fraction.	Strength of alcohol.	Solid matter per cent. of total.
1	46.0 per cent.	43.88
2	59.3 „	23.09
3	75.0 „	10.64
4 (mother-liquor)		22.39
		<hr/> 100.00

Appended are the analyses of each fractional precipitate.

$$\begin{array}{ll} \text{Fraction I.} & [\alpha]_{j3.86} 209.1^{\circ} \\ & \kappa_{3.86} \quad 4.88 \end{array}$$

corresponding to a composition of—

$$\begin{array}{ll} \text{Maltose..} & 8.0 \\ \text{Dextrin..} & 92.0 \\ \hline & 100.0 \end{array} \left. \vphantom{\begin{array}{l} \text{Maltose..} \\ \text{Dextrin..} \end{array}} \right\} \text{which requires } [\alpha]_{j3.86} 210.7^{\circ} \\ \kappa_{3.86} \quad 4.88$$

$$\begin{array}{ll} \text{Fraction II.} & [\alpha]_{j3.86} 206.9^{\circ} \\ & \kappa_{3.86} \quad 6.45 \end{array}$$

$$\begin{array}{ll} \text{Maltose..} & 10.5 \\ \text{Dextrin..} & 89.5 \\ \hline & 100.0 \end{array} \left. \vphantom{\begin{array}{l} \text{Maltose..} \\ \text{Dextrin..} \end{array}} \right\} \text{which requires } [\alpha]_{j3.86} 200.8^{\circ} \\ \kappa_{3.86} \quad 6.45$$

$$\begin{array}{ll} \text{Fraction III.} & [\alpha]_{j3.86} 202.1 \\ & \kappa_{3.86} \quad 13.9 \\ & \hline & 100.0 \end{array}$$

$$\begin{array}{ll} \text{Maltose..} & 22.9 \\ \text{Dextrin..} & 77.1 \\ \hline & 100.0 \end{array} \left. \vphantom{\begin{array}{l} \text{Maltose..} \\ \text{Dextrin..} \end{array}} \right\} \text{which requires } [\alpha]_{j3.86} 200.8^{\circ} \\ \kappa_{3.86} \quad 13.9$$

Fraction IV. The mother-liquor.

$$\begin{array}{ll} & [\alpha]_{j3.86} 193.0^{\circ} \\ & \kappa_{3.86} \quad 24.4 \end{array}$$

$$\begin{array}{ll} \text{Maltose..} & 40.0 \\ \text{Dextrin..} & 60.0 \\ \hline & 100.0 \end{array} \left. \vphantom{\begin{array}{l} \text{Maltose..} \\ \text{Dextrin..} \end{array}} \right\} \text{which requires } [\alpha]_{j3.86} 189.6^{\circ} \\ \kappa_{3.86} \quad 24.0$$

The mean optical and reducing properties of the several fractions correspond very closely with those of the original liquid. In calculating the mean, allowance was of course made for the varying weights of the fractions.

	$[\alpha]_{D}^{25}$	n_D^{25}
Original transformation. . .	202.2°	12.40
Mean of the four fractions. .	203.0	12.05

We now determined the maximum degradation which each fraction underwent with malt-extract at 60°; this, as usual, is expressed in percentages of maltose yielded by the dextrin present in each fraction :—

No. of fraction.	Maltose yielded per cent. of dextrin.
1	60.8
2	70.8
3	87.7
4	93.9

The true mean of these numbers, taking into account the weight of the fractions, is 73.3 against 75.0 yielded by the original dextrin, a result as close as can be expected from the difficult nature of the experiment.

In the two experiments last described, we are confronted with a curious and anomalous fact, for which we were for a long time without an adequate explanation.

In all high-angled transformations, the erythrodextrins, which are undoubtedly highest in the series and of greatest molecular complexity, being comparatively insoluble in weak alcohol, separate out first on fractional precipitation; yet the dextrins which remain in solution in the stronger alcohol are those which yield the largest amount of maltose on treatment with malt-extract.

In our earlier experiments, we attributed this apparent anomaly to over degradation of the more soluble portions; but closer acquaintance with the method of experiment, and the subsequent knowledge which we gained on making our experiments throughout strictly quantitative, negatived this idea, for we found that the degradation of the last and more soluble fractions is far in excess of errors of experiment, and is in fact really *required* in order to make the mean fractional degradation agree with that of the original liquid. It was only when we came to recognise the fact that, besides maltose and dextrin, we had in solution a third body, *maltodextrin*, possessing all the optical and reducing properties of a mixture of maltose and dextrin, but soluble in alcohol and completely hydrated to maltose by malt-extract at 60°, that we arrived at a full explanation of the observed facts. This is a matter which we must leave however for more full discussion at a later part of the paper.

From the fact that all transformations above No. 8 which have been

examined, prove, on fractionation, to be of a mixed character, it is pretty certain that the whole of the starch or starch-products in a transformation are not simultaneously affected to the same extent, but that *some portions are hydrolysed faster than others*. The facts we have brought forward do not disprove the existence of well-marked equations representing the hydrolysis, but the actual changes going on in the liquid at any one instant of time could only be accurately indicated by a series of *simultaneous* equations. One tendency of our recent observations is to show that in practice a sharp line of demarcation cannot be drawn between the equations higher than No. 8. The number of possible equations representing the splitting-up of starch must depend of course on the number of groups of $C_{12}H_{20}O_{10}$ in the starch molecule, always remembering that the extremely well-defined Equation No. 8 corresponds to the hydration of $\frac{4}{5}$ of these groups, no

matter how many there may be. In a former paper, reasons have been given for considering that the starch molecule cannot consist of less than 10 such groups, but it is equally probable that it consists of some simple multiple of 10, which would increase the number of possible equations in the same ratio, and decrease the numerical difference of rotatory and reducing power between them. We have considered it advisable to retain in our table the number of transformations possible in the $10C_{12}H_{20}O_{10}$ theory, as they are amply sufficient to act as fixed points of reference in localising the position of any dextrin in the series of bodies intermediate between soluble starch and maltose.

We have mentioned in an earlier part of this paper that O'Sullivan (Trans., 1879, 770) describes certain dextrans which he has prepared, and which he considers to be those corresponding to his equations C, B, B' and A respectively. He isolated them by partial and frequent precipitations with alcohol from transformations of starch which gave numbers agreeing with these equations, and found, evidently to his surprise, that under the action of malt-extract they did not yield the amount of maltose which the dextrans of the original conversions did whilst in solution with the other transformation-products. There is no doubt whatever, from O'Sullivan's description of the mode of preparation of these dextrans, entailing as it did very frequent precipitation with alcohol, and also from the subsequent action of malt-extract on them, that they consisted of only a portion of the dextrans of the original transformations, and that these transformations, like all others that we have examined, were of a mixed character. The maximum hydrolysis below 62° of his α -dextrin which he prepared from his Equation C products gave 67.8 per cent. of maltose, and consequently corresponded to a position somewhere

between No. 4 and No. 5 of our table, instead of between No. 1 and No. 2, the position it should have occupied had it been truly the dextrin of the C equation. In the same way, β -dextrin I and β -dextrin II, which yielded under the most favourable conditions of temperature only 34.6 per cent. of maltose, must really have occupied a position corresponding nearly to No. 7 of our table, instead of No. 3 and No. 5 respectively.

Mainly on this want of correspondence between the hydrolysis of the separated dextrins and that of the dextrin of the transformation liquid before separation, O'Sullivan is inclined to reject the theory of the molecular degradation of starch, and he asserts his disbelief in the existence of polymeric dextrins. If, however, he had examined the whole of the separated products, *i.e.*, those dissolved by the alcohol, and also those which he rejected in the earlier stages of precipitation as containing malt-extract bodies, he would have found that the separated dextrins *as a whole* do not differ in their behaviour towards malt-extract from those existing in the transformation-liquid before treatment; and he would also have recognised the fact that his original dextrins could not have been homogeneous, nor yet the product of a transformation capable of being represented by a single equation.

The Preparation of Non-reducing Dextrins.

The great difficulty experienced in obtaining, from the products of the hydrolysis of starch, dextrins which are free from any reducing action on Fehling's solution, has given rise to much difference of opinion amongst chemists as to whether pure dextrin has or has not any cupric oxide reducing power. On the one hand, we have the statements of Fürstenberg (*J. pr. Chem.*, **31**, 195), Mulder (*Chemie des Bieres*), Musculus (in his earlier paper of *Ann. Chim. Phys.* [4], **6**, 177), and Brücke (*Wien. Akad. Ber.* [3], **65**, 126), who all deny that dextrin has any action on alkaline copper solution; whilst, on the other hand, Trommer (*Annalen*, **39**, 360), Kemper (*Arch. Pharm.* [2], **115**, 250), Musculus and Gruber (*Bull. Soc. Chim.*, **30**, 54), and other writers, state that dextrin has a distinct reducing action; the last-mentioned chemists having prepared two dextrins which they consider pure, both possessing a reducing power of 12.

The work of O'Sullivan has done much to reconcile these contrary statements by showing that the reducing action is due to the admixture of a small quantity of maltose which clings tenaciously to the dextrin, and from which it can only be separated with difficulty. O'Sullivan showed that by a preliminary fermentation of the maltose, and very frequent precipitation with alcohol, it is possible to diminish

the reducing power of a dextrin to an amount varying from $\kappa 2.5$ to $\kappa 0.5$, but he does not appear ever to have prepared a dextrin entirely free from action on Fehling's solution.

By fermenting with yeast, and subsequent precipitation with alcohol, we have always found it extremely difficult to prepare a dextrin having a less reducing power than 4 or 5, unless the starch-transformation has been pushed to its lowest limit. It is evident from the experimental results we have described that it would be hopeless, by any process entailing very frequent precipitation with alcohol, to attempt to prepare a dextrin which should correspond in position and properties with those of the impure dextrin, unless the latter happens to be homogeneous to commence with. We must, therefore, look to some other process than the above to attain the desired end.

When a dextrin still containing maltose is submitted to the action of Fehling's solution, a little consideration will tell us that whilst the maltose is attacked the dextrin is not degraded, for were this latter the case the additional maltose produced during degradation would reduce a further quantity of copper liquid, and we should obtain analytical results which would not correspond with the optical examination. It seems clear, therefore, that if the dextrin could be recovered from the Fehling's solution we should have it without reducing properties, and in the same molecular state as the original dextrin taken.

Attempts to carry out this separation were so unsuccessful, and of such an unpromising nature, that they were soon abandoned, and we looked for another oxidising agent which might answer the purpose.

In 1874, Bondonneau (*Bull. Soc. Chim.*, **21**, 50 and 149) described a new method for the preparation of pure dextrin. It consisted in treating ordinary dextrin in solution with cupric chloride and a sufficient quantity of caustic soda to redissolve the precipitate first formed. On boiling for half an hour, he states that the sugar is completely destroyed, and that the liquid after filtration (in order to separate the cuprous chloride) and acidifying with hydrochloric acid, yields, on precipitation with alcohol, pure dextrin, or at any rate a body not containing more than 0.002 per cent. of sugar.

Bondonneau does not appear to have been very successful himself in the application of this method, judging from the fact that in the following year (*Bull. Soc. Chim.*, **23**, 98) he describes a dextrin, prepared from starch by diastase, and purified by his method, which possessed an optical activity of $[\alpha]_{176^{\circ}}$.

We have made frequent use of Bondonneau's method, but not successfully, as will be seen from the following experiments:—

(1.) A transformation of starch with malt-extract, which gave

numbers for the mixed products of $[\alpha]_{j3.86} 202.7^\circ$, $\kappa_{3.86} 14.3$, was, after one or two precipitations with alcohol, treated by the cupric chloride method. A dextrin was finally obtained, giving—

$$\begin{array}{r} [\alpha]_{j3.86} 213.7 \\ \kappa_{3.86} \quad 0.53 \end{array}$$

(2.) A starch-transformation was pushed to nearly the No. 8 limit, and after partial separation by one or two precipitations with alcohol, the insoluble portion was treated by Bondonneau's method, after which the dextrin gave the following numbers:—

$$\begin{array}{r} [\alpha]_{j3.86} 199.5^\circ \\ \kappa_{3.86} \quad 2.0 \end{array}$$

The low angle in this case was due to the presence of about 6 per cent. of inactive bodies, consisting mainly of sodium chloride, and also of a little of the malt-extract substances.

(3.) A transformation, giving for the mixed products (corrected) $[\alpha]_{j3.86} 182.4^\circ$, $\kappa_{3.86} 32$, was precipitated five times with alcohol.

A portion of the resulting dextrin, on complete degradation with malt-extract at 60° , yielded 36.2 per cent. of maltose. The principal portion, after treatment by the cupric chloride method, gave—

$$\begin{array}{r} [\alpha]_{j3.86} 205.1^\circ \\ \kappa_{3.86} \quad 2.03 \end{array}$$

and was found not to be in the slightest degree hydrolysed by malt-extract at 60° , after this treatment.

This method of purification has yielded unsatisfactory results in our hands, inasmuch as we have never been able by its means to prepare a dextrin entirely free from reducing power, and moreover the *dextrins are degraded* during the process, and consequently do not correctly represent those originally operated on. This degradation of the dextrin is well shown in Experiment 3, and was always observed when specially looked for.

In 1882, Wiley (*Chem. News*, 46, 175) proposed a new application of Knapp's mercuric cyanide solution for the analysis of mixtures of maltose, dextrose, and dextrin. An original feature in the proposed new method consisted in destroying all the maltose and dextrose by means of alkaline mercuric cyanide, and after acidifying determining the dextrin by the residual optical activity of the solution. Following up the hint contained in this paper of Wiley's, we have successfully applied a modification of the alkaline mercuric cyanide method to the purification of the starch dextrins, and have thus been able to obtain them quite free from cupric oxide reducing power, and, what is of more importance, in the same molecular state as that in which they occur in the unpurified dextrin. The manner in which this has been

accomplished will be better understood from the following particulars of actual experiments.

A dextrin prepared from a transformation of starch with malt-extract by precipitation with 60 per cent. alcohol, was partially purified by several treatments with alcohol* of the same strength. A dextrin was in this way obtained containing—

Maltose	2.59	} which requires $[\alpha]_{j3.86} 211.3^\circ$ $\kappa_{3.86} 1.58$
Dextrin	96.02	
Malt-extract bodies ..	1.39	
	<hr/> 100.00	

To a solution of this dextrin was added a slight excess of a solution containing equal weights of mercuric cyanide and caustic soda, and the whole was warmed until the reduction was complete. The solution was cooled, and the reduced mercury was filtered off. The filtrate was very slightly acidified with hydrochloric acid, and hydric sulphide passed into it to precipitate the slight excess of mercury salt. After the mercury sulphide had been filtered off, ammonia was added in slight excess, the whole evaporated to a syrup, dissolved in hot water, filtered, and the filtrate precipitated with alcohol of 60 per cent.*

The numbers given on analysis were—

$$\begin{array}{r} [\alpha]_{j3.86} 209.4^\circ \\ \kappa_{3.86} 0.0 \end{array}$$

corresponding to a composition of—

Dextrin.....	96.9
Inactive matter	3.1
	<hr/> 100.0

the inactive matter in this case consisted almost entirely of sodium chloride.

On degradation with malt-extract at 60°, the purified dextrin, corrected for the salts present, gave 51.5 per cent. of maltose, against 49.5 yielded by the original dextrin, hence we see that the dextrin has been unaltered by the mercury cyanide process. The small difference falls well within the limits of experimental error, and is in fact in the opposite direction to that which would have been observed had the dextrin really undergone any change.

* This was in order to avoid as much as possible a separation of the dextrans, which would certainly have taken place if alcohol of a different strength from that used in the original preparation had been employed.

That the low angle obtained in the above experiment was really due to an admixture of salts, and not to any change in the optical activity of the dextrin, was shown as follows :—

A partially purified dextrin, giving $[\alpha]_{\text{D}}^{20} 212.3^\circ$, $\kappa_{\text{D}}^{20} 1.3$, was treated by the mercuric cyanide method, a definite volume of a solution of known sp. gr. having been taken. After treatment, the liquid, which gave no reduction with Fehling's solution, was made up to a definite volume and examined in the polariscope. The reading calculated on the quantity of pure dextrin in the original substance, gave—

$$\begin{array}{r} [\alpha]_{\text{D}}^{20} 215.9 \\ \kappa_{\text{D}}^{20} 0.0 \end{array}$$

It will be observed that the optical activity of pure non-reducing dextrin so obtained corresponds almost exactly with $[\alpha]_{\text{D}}^{20} 216.0^\circ$, the value we deduced from our experiments on the transformations of starch.

Is any other Substance besides Maltose and Dextrin formed during the Transformation of Starch by Diastase ?

Two very distinct bodies have been separated from the products of transformation of starch by diastase, one the crystalloid *maltose*, having a reducing power of $\kappa_{\text{D}}^{20} 61$, and an optical activity of $[\alpha]_{\text{D}}^{20} 150^\circ$; the other colloidal *dextrin*,* having no reducing power, and an optical activity of $[\alpha]_{\text{D}}^{20} 216$.

Since the optical and reducing properties of any transformation taken as a whole, or of the products fractionated to any desired extent with alcohol, always give results, both with the polariscope and with the alkaline copper liquid, which are capable of being expressed exactly in terms of maltose and dextrin, it might be imagined that there could not be much room to suspect the existence of a third body. A little consideration, however, will show that there might be present a third body, differing in many important respects from maltose and dextrin, providing only it fulfilled the somewhat improbable condition that it should have an optical activity and reducing power corresponding to a mixture of those two substances.

We shall now proceed to indicate the steps by which we have been gradually forced to admit that a third body really does exist under certain conditions amongst the starch-transformation products.

When it is wished to prepare maltose from starch, it is necessary, in order to bring the sugar into a readily crystallisable form, to push

* The term is used here generically, and includes of course all the polymeric dextrins.

the reaction to the lowest possible limit of hydrolysis. From transformations much higher than No. 8, it is, on the other hand, extremely difficult to get the maltose to crystallise out in any quantity at all commensurate with the cupric oxide reducing power of the products, and this difficulty becomes greater the higher in the series the transformation is. As the difficulty of crystallising the maltose increases, so much the greater difficulty is at the same time experienced in fermenting it. If the transformation has run down completely to No. 8 limit, the whole of the maltose within 1 per cent., or even less, may be made to ferment; but from the higher transformations, as we shall presently show, we can prepare solutions which, judging from their reducing power, appear to contain from 30—40 per cent. of maltose in the solid products, and yet which are *perfectly unfermentable* with ordinary yeast.

These, and certain other considerations, led us early in the history of these investigations to the belief that maltose is capable of existing in two distinct forms, the one crystallisable and easily fermentable, the other possessing, indeed, the same optical and reducing powers, but forming with dextrin a combination soluble in alcohol, not decomposable into its constituent maltose and dextrin by ordinary solvents, sufficiently stable to withstand contact with yeast, but readily converted into freely crystallisable and fermentable maltose by the action of a little unheated malt-extract.

The following experiments may be quoted in proof of this proposition:—

A transformation yielding $[\alpha]_{j3.86} 192.9^\circ$, $\kappa_{3.86} 24.9^\circ$, was first precipitated with strong (90 per cent.) alcohol.

The residue had $[\alpha]_{j3.86} 190^\circ$, and $\kappa_{3.86} 17.8^\circ$, and besides maltose and dextrin, contained 3.2 per cent. of malt-extract bodies. This was treated again with hot alcohol of 70—80 per cent., and the soluble portions taken for experiment. These had—

$[\alpha]_{j3.86} 185.3^\circ$ $\kappa_{3.86} 24.3$, corresponding to a composition of	{	Maltose.....	39.8
		Dextrin	58.1
		Inactive matter.	2.1
			<hr/> 100.0

On degradation with malt-extract at 60° , the contained dextrin yielded 70 per cent. of maltose.

An aqueous solution was made containing 12.663 grams of solids per 100 c.c., which was set to ferment at 28° C. with 1.2 gram per 100 c.c. of washed yeast, partially dried between folds of blotting-paper. The ferment used was the ordinary *Saccharomyces cerevisiae* (high fermentation) of the Burton type. From the percentage com-

position of the substance taken, the solution ought to have contained 5.039 grams of maltose per 100 c.c.

A slight fermentation set in at once, but at the end of three or four days had completely ceased. On the ninth day, the liquid was analysed, and it was found that it apparently still contained 3.687 grams of maltose per 100 c.c., 1.352 gram having disappeared by fermentation.

The question now arises, why should the action of the yeast so completely cease, when only one quarter of the total apparent quantity of maltose present has been fermented, and when the total solids still seem to contain 32 per cent. of that sugar? That all the conditions favourable to the growth of the yeast and the exercise of its functions were present except the all important one of a fermentable carbohydrate, was shown in the following way:—

A small quantity of *maltose* was added to the fermented liquid, still containing its yeast, at the rate of 0.69 gram per 100 c.c. A brisk fermentation at once commenced, but as speedily subsided, and once more entirely ceased, the optical activity of the solution indicating that the maltose added had all disappeared, but that *nothing else had been affected*. After a few days a second quantity of maltose was added, at the rate of 1.22 gram per 100 c.c. Again the fermentation commenced, but was entirely completed in four days more. A complete analysis of the liquid was once more made, and the amount of maltose which had disappeared per 100 c.c. since the first addition, was estimated by the increase in alcohol,* and found to be 2.02 grams against $0.69 + 1.22 = 1.91$ gram actually added.

The solids after fermentation gave on analysis 31.6 per cent. maltose, as deduced from their optical and reducing properties, against 32 per cent. before fermentation, a proof that the 3.687 grams of the cupric oxide reducing substance proper to the starch-products had not been touched, notwithstanding the brisk fermentation produced by the added maltose. At the close of this stage of the experiment, the products after fermentation gave $[\alpha]_{D, 20}^{25} 189.2^\circ$ and $\kappa_{D, 20} 19.3$, against $[\alpha]_{D, 20}^{25} 189.9^\circ$ and $\kappa_{D, 20} 19.7$ before the addition of the maltose. It was also found that on complete degradation of the dextrin after fermentation 100 parts yielded 70 parts of maltose, which is exactly the amount given by the dextrin at the commencement of the experiment, and hence the dextrins have not been degraded by the fermentation.† The residual liquid after fermentation was

* This method, if carefully carried out, with a proper allowance for the non-volatile products of fermentation, is capable of giving very accurate results, even with very small quantities of the sugar. In this and similar experiments, the results were further checked with the polariscope and Fehling's solution.

† It must be noted that in this experiment there was no alteration in the type

filtered, evaporated, and submitted to treatment once more with alcohol, but this time *little or no further separation could be effected with the solvent*, both precipitate and filtrate bodies having as nearly as possible the same optical activity and reducing power, viz., $[\alpha]_{j3.86} 192.2^\circ$, $\kappa_{3.86} 19.3$.

Let us now examine, for the sake of comparison, what takes place when *artificially prepared mixtures* of maltose and dextrin are (1) submitted to fermentation, (2) treated with alcohol.

A dextrin was taken which had been partially purified by Bon-donnean's method, and which yielded 44 per cent. of maltose on degradation with malt-extract at 60° . This gave—

$$\begin{array}{r} [\alpha]_{j3.86} 212.0^\circ \\ \kappa_{3.86} \quad 0.53 \end{array}$$

A solution of this dextrin was made and mixed with another solution of carefully purified maltose, the optical activity and reducing power of which had been verified. The mixed solutions were boiled, evaporated to a syrup, and made up to 250 c.c. The properties of the mixture were—

$$\begin{array}{r} [\alpha]_{j3.86} 186.2^\circ \\ \kappa_{3.86} \quad 25.7 \end{array}$$

(1.) 130 c.c. of the solution were set to ferment at 25° , with 1.5 gram of washed and partially dried yeast. Fermentation was vigorous and rapid. At the end of 12 days it had entirely ceased, and the residue, after the proper corrections were made, was found to have—

$$\begin{array}{r} [\alpha]_{j3.86} 207.3^\circ \\ \kappa_{3.86} \quad 1.1 \end{array}$$

(2.) 105 c.c. of the same solution was evaporated to a syrup, and then precipitated and digested *only once* with alcohol of 85 per cent.

Analysis of the residue gave—

$$[\alpha]_{j3.86} 205.8^\circ,$$

of the matter in solution, $[\alpha]_{j3.86} 158.8^\circ$.

Nothing could be more striking than the difference in behaviour between the products from high transformations, which are soluble in alcohol of 70—80 per cent., and artificially prepared *mixtures* of dextrin and maltose having about the same value for $[\alpha]_j$ and κ ; both as regards their behaviour towards yeast and the results they give when treated with alcohol. This last experiment alone, we consider, sufficiently proves that the cupric oxide reducing body of the first

of the yeast cells. From first to last, they consisted of the primary forms of *Saccharomyces cerevisiae*. The importance of this fact will be evident a little later on.

solution, if it be maltose, must be in a very different state from the freely fermentable and freely separable maltose of the second solution.

We will give one more experiment of a similar nature to the last, merely remarking that it is one of many, all giving results of exactly the same kind.

A starch-conversion was made, giving for the mixed products—

$$\begin{array}{r} [\alpha]_{D^{20}} 198.2^\circ \\ \kappa_{D^{20}} 14.08 \end{array}$$

A solution of these of a sp. gr. 1051.59 and containing 12.538 grams of solids per 100 c.c., was set to ferment with yeast at 28° for several days. After nine days, when all signs of fermentation had ceased, it gave on analysis :—

$$\begin{array}{r} [\alpha]_{D^{20}} 200.6^\circ \\ \kappa_{D^{20}} 10.9, \text{ corresponding to} \end{array} \left\{ \begin{array}{lr} \text{Maltose} \dots\dots\dots & 17.8 \\ \text{Dextrin} \dots\dots\dots & 80.5 \\ \text{Inactive matter} \dots\dots & 1.7 \\ \hline & 100.0 \end{array} \right.$$

1.028 gram of maltose per 100 c.c. had disappeared, leaving apparently 2.231 grams in solution, which however refused to ferment any further. Pure maltose was now added at the rate of 1.767 gram per 100 c.c., and the fermentation at once recommenced vigorously and continued for two or three days. At the end of 14 days, the liquid was again analysed, the solids giving—

$$\begin{array}{r} [\alpha]_{D^{20}} 200.6^\circ \\ \kappa_{D^{20}} 10.6, \text{ corresponding to} \end{array} \left\{ \begin{array}{lr} \text{Maltose} \dots\dots\dots & 17.4 \\ \text{Dextrin} \dots\dots\dots & 80.8 \\ \text{Inactive matter} \dots\dots & 1.7 \\ \hline & 100.0 \end{array} \right.$$

which is practically the same composition as before the addition of the maltose. The amount of maltose which had been fermented the second time was calculated from the alcohol formed, with the following result :—

Maltose added per 100 c.c.	1.767 gram
Maltose fermented	1.789 „

It is quite certain from this experiment again, that the cupric oxide reducing substance left in the solution after the fermentation of the starch-products, must be different in character from the free crystallisable maltose subsequently added. It is also certain that the dextrins have undergone little or no degradation during the process. since, in this particular experiment, they were found to yield, with

malt-extract at 60°, 79·2 per cent. of maltose before, and 76·1 after fermentation.

If, after the fermentation of any of the solutions such as were made use of in the last experiment, instead of maltose or any other fermentable sugar, we add merely a drop of malt-extract, fermentation recommences with more or less rapidity, the cupric oxide reducing substance becomes capable of fermentation, and the dextrins are at once degraded and also yield their share of fermentable maltose.

This action of malt-extract in promoting the complete fermentation of the dextrins was first noticed by Payen, and subsequently by Musculus (*Ann. Chim. Phys.* [4], 6, 177); but the latter has erroneously stated that the same action takes place even if the malt-extract is previously boiled.

In a previous part of the paper, we have had to refer to the apparent existence in the alcoholic solutions of the fractionated starch-products (more especially when these are derived from high transformations) of a dextrin which, on treatment with malt-extract at 60°, gives an amount of maltose equal to from 90 to 95 per cent. of its weight. This *quasi-dextrin is invariably found associated with the unfermentable and uncrystallisable maltose above referred to, and cannot be separated from it by fractionating further with alcohol, nor yet by the action of *Saccharomyces cerevisiæ*. The two bodies are, in fact, undoubtedly in a state of combination, although possessing the optical and reducing properties of mere mixtures of maltose and dextrin.*

In the year 1879, Herzfeld stated ("Ueber Maltodextrin") that he had found it impossible to crystallise maltose from starch conversions carried on by diastase at 70°, and he also described a substance which he had obtained, when working under those conditions, which was soluble in alcohol, and which he purified by frequent treatment with that solvent. He looks upon this substance as a product of hydration,* intermediate between achroodextrin and maltose, and, believing that it may consist of a combination of two dextrin-groups with a sugar-group, thus:— $\left\{ \begin{array}{l} C_6H_{10}O_5 \\ C_6H_{10}O_5, \\ C_6H_{12}O_6 \end{array} \right.$ he gives it the name of *maltodextrin*.

According to Herzfeld, the specific rotatory and reducing powers of maltodextrin are as follows:—

$$\begin{array}{c} [\alpha]_D 171\cdot6^\circ \\ \kappa \ 23\cdot5 \end{array}$$

* It must be remembered that Herzfeld is opposed to the theory of the molecular splitting up of starch, and considers that maltose is reached by successive acts of hydration through amylo-, erythro-, and achroo-dextrin, and maltodextrin.

Since, however, Herzfeld has taken 2 parts of Cu, or 2.362 CuO as being equivalent to 1 part of dextrose, instead of 1.760 Cu, or 2.205 CuO, his numbers representing the reducing power require correcting in order to admit of a comparison with our own. The corrected numbers for Herzfeld's maltodextrin thus become—

$$[\alpha], 171.6^{\circ}$$

$$\kappa \ 26.7$$

Even when the correction is made, this body does not conform to the test of purity which we have established, by which all separated portions of a starch transformation must give values of $[\alpha]$, and κ , which will work out for maltose and dextrin only. Judging from the value of κ alone, Herzfeld's maltodextrin ought to be made up of 43.7 per cent. of maltose, and 56.3 per cent. of dextrin; but the optical activity of such a mixture should be 187.1° instead of 171.6° as given. The difference is doubtless due to impurities derived from the unnecessarily large quantity of malt-extract employed in the conversion.

Notwithstanding the above remarks, we are fully convinced that Herzfeld has had in his hands, but in an impure state, the body which we have found amongst the more soluble portions of starch transformation-products treated with alcohol, and which we have looked upon as having certain properties indicating a combination of maltose and dextrin. In one particular, Herzfeld's description is totally at variance with our observation. He states that his maltodextrin is *readily and completely* fermentable, whereas our substance is unfermentable by the ordinary *Saccharomyces cerevisiæ* of the "high fermentation" until it is further hydrated, either by a little malt-extract or by the slow action of certain forms of yeast, in a manner to be described shortly.

We shall in future adopt Herzfeld's name of *maltodextrin* for our unfermentable, cupric oxide reducing substance, as it is in several respects a happy one; but we certainly cannot accept his ideas as to the place which maltodextrin occupies in the series of starch transformation-products. The theory of successive hydration from starch to maltose, through a series of bodies *metameric* with starch, is one which is capable of including a less number of facts than any which has been brought forward; whereas the theory of the hydrolysis of the starch molecule, with the simultaneous production of maltose and a series of *polymeric* dextrins, as propounded by Musculus and Gruber, and also by one of us in conjunction with J. Heron, is, when somewhat expanded, capable of including all the facts which are at present known.

The preparation of *maltodextrin* in a state of perfect purity is

attended with some difficulty; for although this body is more soluble in alcohol than the dextrins, yet some of these latter are not absolutely insoluble in alcohol of 85 per cent. The following is the method which up to the present time we have found the most successful:—A *diastase* is first freshly prepared from the most actively diastatic malt* which can be obtained. As small a quantity as possible of this diastase is used in making a starch transformation at 60–65°, arresting the action as soon as the optical activity of the products has fallen to $[\alpha]_{D^{20}} 198^\circ$ or thereabouts. The solution, after boiling, is evaporated down to about sp. gr. 1060·0, and set to ferment at 28–30° with a small quantity of washed yeast, *Saccharomyces cerevisiae* of the high fermentation. The free maltose, amounting in such a case as we are considering to from 7 to 8 per cent. of the total starch-products, can in this way be destroyed in a few days if proper care is taken. After the fermentation is complete, the clear liquid is poured off the yeast through a filter and evaporated to a syrup, which is digested for a day or two with boiling alcohol of 90 per cent † with frequent agitation. This treatment removes the greater part of the non-volatile products of fermentation, which amount to nearly 5 per cent. on the quantity of maltose fermented. The strength of alcohol used is then reduced to 85 per cent., and, after digestion, this is poured hot off the residue, and on distillation of the spirit, leaves maltodextrin, which, by a little further treatment with alcohol, can be obtained in a pure state. In this way we have prepared it, possessing the following properties:—

$$\begin{array}{r} [\alpha]_{D^{20}} 193\cdot6^\circ \\ \kappa_{D^{20}} 20\cdot7 \end{array}$$

If it consisted of a mixture of maltose and dextrin, the composition would be represented exactly by—

$$\left. \begin{array}{r} \text{Maltose.} \quad 33\cdot9 \\ \text{Dextrin.} \quad 66\cdot1 \\ \hline 100\cdot0 \end{array} \right\} \text{requiring } \begin{array}{r} [\alpha]_{D^{20}} 193\cdot6^\circ \\ \kappa_{D^{20}} 20\cdot7 \end{array}$$

That maltodextrin does not contain maltose, *as such*, is shown by the fact that it is absolutely unfermentable by ordinary *Saccharomyces cerevisiae* of the high fermentation, and that it is not separable into its apparent constituents by treatment with alcohol. Moreover, on treatment with malt-extract at 50–60°, *its apparent dextrin con-*

* For this purpose it is better to use a malt which has been air-dried at a temperature not exceeding 30–32° C.

† By this is meant that the mixed syrup and alcohol contain 90 per cent. by volume of absolute alcohol.

stituent is converted completely into maltose. This is a further proof, if any were required, that we are not dealing with a *mixture* of maltose and dextrin, for as we have before shown, all the true dextrins hitherto isolated from the starch-products yield, on complete degradation with malt-extract at 50—60°, a residue of the lowest No. 8 dextrin, dependent in amount on their position in the series; whereas the dextrin-group of maltodextrin is rapidly and completely converted into maltose by a similar treatment.

If we suppose maltodextrin to consist of some sort of combination of maltose and dextrin, the simplest formula that can be assigned to it from the foregoing analysis is $\left\{ \begin{matrix} C_{12}H_{22}O_{11} \\ (C_{12}H_{20}O_{10})_2 \end{matrix} \right\}$; that is, a maltose-group united with two amylin- or dextrin-groups, each constituent group retaining its optical and reducing properties. Such a body would have the following optical activity and reducing power:—

$$\begin{array}{l} [\alpha]_{D^{20}} 86.193.1^\circ \\ \kappa_{3-88} \quad 21.1 \end{array}$$

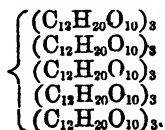
numbers very close to those actually observed.

In a previous paper by one of us (Brown and Heron, *loc. cit*) reasons have been given for assigning to soluble starch the formula $10C_{12}H_{20}O_{10}$, and we have supposed the hydrolysis of this complex molecule, under the action of malt-extract, to be effected by the successive removal of a single group of $C_{12}H_{20}O_{10}$ by its hydration into maltose, the remaining groups of $C_{12}H_{20}O_{10}$ forming in each case a dextrin, having a molecule of decreasing complexity as the hydrolysis of the starch becomes more complete.

It will now be seen that this hypothesis in its present form is not sufficiently comprehensive to include the new facts we have brought forward, which support the idea that the hydration of the separated $C_{12}H_{20}O_{10}$ -groups to maltose takes place by stages.

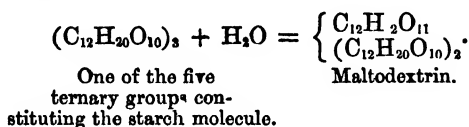
We venture to suggest the following extension of the above idea as a provisional explanation of the facts. As a working hypothesis we have found it very useful, and we consider that it is a closer approximation to the truth than has been hitherto put forward, although it will doubtless require further development as we gain a more intimate knowledge of this very difficult subject.

We believe that the molecule of starch cannot be looked upon as consisting of less than five times the group $(C_{12}H_{20}O_{10})_5$, thus—

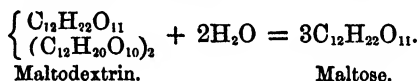


We still suppose that the action of malt extract in hydrolysing the above molecule consists in a successive hydration and removal of the $(C_{12}H_{20}O_{10})_3$ groups, leaving a dextrin residue of decreasing complexity until the last remaining group of $(C_{12}H_{20}O_{10})_3$ is reached, which is the dextrin of our No. 8 equation, to which such frequent reference has been made, and which does not undergo any further change except a comparatively slow process of hydration.

The removal of each $(C_{12}H_{20}O_{10})_3$ group is, however, accomplished prior to its complete hydration, the ternary group being split off in the form of *maltodextrin*, when one only of its amylin sub-groups has been hydrated, thus:—



Malt-extract which has not been heated higher than 65° , rapidly effects the complete conversion of the maltodextrin into maltose by the hydration of the remaining amylin sub-groups, thus—



It is quite possible that this latter change may also be brought about by two successive steps, but up to the present we have not been able to obtain any evidence pointing to the existence amongst the starch-transformation products of a combination corresponding to $\left\{ \begin{array}{l} (C_{12}H_{22}O_{11})_2 \\ (C_{12}H_{20}O_{10}) \end{array} \right.$, which would have an optical activity of $[\alpha]_{D, 20} 172.7^\circ$, and a cupric oxide reducing power of $\kappa_{0.88} 39.9^\circ$.*

As we are engaged in fully studying the properties of maltodextrin, we must defer a further detailed description of this body to another time. Sufficient has, however, been said for the present to indicate that we have amongst the products of the transformation of starch by diastase a body, the existence of which has previously been all but unrecognised, and one which must play a very important part in all those technical processes which are dependent on the conversion of starch and the subsequent fermentation of the products.

It is certainly a remarkable fact that the optical activity of malto-

* Maltodextrin may be looked upon, from one point of view, as a *maltaan*, i.e., maltose less the elements of water, and it is possible that it may be found to be analogous to Scheibler's *dextran* (*Zeitschr. für Rübenzucker Industrie*, 1874, 309) and Lippemann's *lavulan* (*Ber.*, 14, 1509), when more is known about the origin of these two last-named bodies.

dextrin should be the mean of that of its apparent constituents, especially when we consider how readily the specific rotatory power of organic substances is altered by a slight chemical or even physical change; but it is, perhaps, not more remarkable than the equally certain fact that the polymeric dextrins and soluble starch all possess the same specific rotatory power.

We have had occasion to refer to the fact that maltodextrin and the dextrins are not acted on by the ordinary *Saccharomyces cerevisiæ* of the "high fermentation," but that a little malt-extract hydrolyses them, and thus affords a plentiful supply of free maltose to the yeast.

There is yet another method by which maltodextrin and the dextrins can be fermented, to which reference must now be made, especially as it is a natural process of great practical importance. It will be better understood from the following experiment.

The products of a conversion of starch with malt-extract, giving an angle of $[\alpha]_{D^{20}} 190.1^\circ$, were evaporated and digested twice with strong alcohol, the optical activity of the residue being $[\alpha]_{D^{20}} 191.2^\circ$. A solution of these starch-products was made, of sp. gr. 1.0995, containing maltose, maltodextrin, and several achroodextrins, and was set to ferment at 30° .

The fermentation, which was very brisk at first, ceased in three days, when the free maltose had all disappeared.

The apparent composition of the solution was—

$[\alpha]_{D^{20}} 194.2^\circ$ $\kappa_{D^{20}} 17.7$, corresponding to	{	Maltose.....	29.0
		Dextrin.....	69.7
		Inactive matter ..	1.3

On degradation with malt-extract at 60° , 100 parts of the dextrin yielded 66.8 parts of maltose.

The alcohol was driven off by evaporation, without any change being brought about, and the syrup was redissolved in water, and made up to sp. gr. 1.093, corresponding to 24.093 grams of solids per 100 c.c. According to the above analysis these were made up of—

Maltose.....	6.986	grams
Dextrin.....	16.792	"
Inactive matter.....	0.315	"
		<hr/> 24.093

Some yeast was again added to this solution, the solid matter of

which, it will be remembered, had already been fermented once before, and the whole was submitted to a temperature of 30°.

The solution was narrowly watched, and a little of the sediment examined daily under the microscope.

The original yeast cells, consisting of the *Saccharomyces cerevisiæ* of the "high fermentation," not finding any free maltose in the solution (although judging from the reducing power there should have been nearly 7 grams per 100 c.c.), shrivelled up and to all appearances died. At the end of six or seven days, not a trace of fermentation having previously been observed, a few cells of *Saccharomyces ellipticus* and *pastorianus* began to appear. Concurrently with this alteration in microscopical appearance, fermentation commenced, at first with extreme slowness, but gradually becoming much more rapid as the new forms* of *Saccharomyces* increased in abundance.

At the end of forty days, when the experiment was stopped, fermentation was still going on slowly.

The amount of maltose which had fermented was determined in two ways: (1) by the decreased sp. gr. of the solution after distilling off the alcohol, and (2) by estimating the alcohol formed, and calculating it as maltose, due allowance being made in each case for the non-volatile products of fermentation.

Method (1) gave a disappearance of 14.398 grams maltose per 100 c.c.

" (2) " " " 14.410 " " "

Now when we consider that the original solution only contained equal to 6.986 grams maltose per 100 c.c., it is evident that the remaining 7.414 grams must have been produced at the expense of the dextrin. We should consequently expect to find the residual dextrin degraded, which in fact it was, as 100 parts at the close of the experiment yielded with malt-extract at 60° only 25.7 parts of maltose, against 66.8 before fermentation.

Hence the average constitution of the dextrin has been lowered from a point corresponding closely to No. 4 of the table, to a point considerably below No. 7. In this case the secondary forms of *Saccharomyces* have been able to bring about a change which the original *S. cerevisiæ* could not; but it would not be safe to assume that typical

* These secondary forms of *Saccharomyces*, which to a great extent carry on the "secondary," or "after fermentation" of our high fermentation beers, are not genetically connected with the *S. cerevisiæ* of the principal fermentation (Hauptgährung) which makes up the larger part of brewers' yeast, but are derived from the more or less numerous cells of *S. pastorianus*, &c., contained in this. The presence of these secondary alcoholic ferments, which are all "low fermentation" yeasts, is not recognised until the conditions of cultivation are rendered more favourable to them than to the more dominant form.

S. cerevisiæ is incapable, under all conditions, of hydrolysing the dextrins and maltodextrin, and thus supplying itself with food. Such is certainly not always the case, although the secondary forms, which are "bottom ferments," seem to possess this power in a high degree, and are capable of exercising it under conditions of nutrition, &c., which are unfavourable to the *S. cerevisiæ*, and under which the latter are incapable of exercising any hydrolytic action.*

The hydrolysis of the dextrins under the action of certain alcoholic ferments is most likely brought about by the living cells of the yeast modifying small quantities of albuminoids which are always present, and so producing an amylolytic or diastatic ferment. It has already been shown by one of us (Brown and Heron, this Journal, 1879, i, 596) that the comparatively inactive albuminoids of unmalted barley may be rendered much more amylolytic by submitting them for a few hours to the action of yeast at 30°.†

In conclusion, we must remark that in order to keep this paper within reasonable limits of space, it has been found necessary to include only typical experiments bearing upon each separate point. The data in our possession consist of many hundreds of analyses, all distinctly pointing to the general correctness of the views we have expressed.

Since the completion of the above paper we have further convinced ourselves of the homogeneity of maltodextrin by submitting it to *dialysis*.

Maltodextrin is slowly diffusible, and passes through the septum with all its properties unaltered; whereas from a mere mixture of maltose and dextrin the highly diffusible crystallised maltose is readily separable from the dextrins, which are all highly colloidal.

We add a brief summary of the principal conclusions at which we have arrived.

* It is possible that in this differential action of the various species or varieties of *Saccharomyces*, lies an explanation of the difference of opinion between Herzfeld and ourselves with regard to the fermentability of maltodextrin.

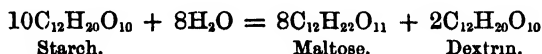
† The degradation of the dextrins and the hydration of maltodextrin, under the action of yeast and malt-extract separately or combined, explain many phenomena observed during the fermentation of beer and distillers' worts; but this is scarcely the place to discuss matters of so purely technical a nature: suffice it to say, that the stimulating influence of malt-flour, &c., which is sometimes added to increase the rapidity of fermentation, or (as in the secondary fermentation of beer) to renew an action which has wholly or partially ceased, is due to the hydrolytic power such bodies possess. By the slow exercise of this power they break down the complex dextrins, and hydrate the maltodextrin, thus affording to the yeast a supply of maltose in a state fit to be seized upon and broken up. The action of all these stimulating agents is consequently *indirect*, and has little or nothing to do with the insignificant amount of yeast-food introduced with them, as is often erroneously imagined.

1. When starch-paste is acted on by malt-extract at any temperature above 40° , the specific rotatory power and cupric oxide reducing power of the mixed products are such as would be accounted for by the presence only of maltose, and a non-reducing dextrin of $[\alpha]_{D^{20}} 216^{\circ}$.

2. On fractionating such a transformation with alcohol, the optical and reducing properties of the several fractions all agree in giving results which can also be interpreted in terms of maltose and dextrin only.

3. We thus establish a criterion of purity for any separated portion of the transformation-products, and we ascribe any apparent departure from this rule as regards substances described by other observers, as due either to the presence of impurities or to errors of determination.

4. The tendency of all starch-transformations, when subsequently acted on by malt-extract at $50-60^{\circ}$, is rapidly to attain a state of equilibrium which is represented by the following equation, No. 8 of our series:—



When the whole of the products derived from the starch are taken together, this reaction corresponds to an optical activity of $[\alpha]_{D^{20}} 162.6^{\circ}$, and $\kappa_{D^{20}} 49.3$; and to a percentage composition of maltose 80.9, dextrin 19.1.

5. The degradation of all the higher transformations down to this point is due to the hydrolysis of the more complex polymeric dextrans and maltodextrin.

6. The dextrin and maltodextrin can be submitted to solution in water, evaporation, and frequent precipitation with alcohol, without being hydrolysed.

7. This is proved by the fact that the transformation-products, after such treatment, when subsequently fractionated with alcohol, yield fractions with a mean value of $[\alpha]_D$ and κ coinciding with that of the original solution. It is further proved also by 8.

8. The mean maximum degrading effect of malt-extract at $50-60^{\circ}$, acting on the separate portions of a saccharification respectively soluble and insoluble in alcohol, or on fractional portions necessarily separated with alcohol, is the same in amount as the effect exercised, *ceteris paribus*, by the malt-extract on the original starch-products before separation. Hence the separated dextrans have not, as stated by O'Sullivan, different properties as regards their behaviour with malt-extract from those they possess when in solution with the other transformation-products formed simultaneously with them.

9. It also follows that it is possible by submitting a separated

dextrin or mixture of dextrans to the action of malt-extract at 50—60°, and determining the percentage of maltose they yield, to ascertain the actual or mean position of the dextrin in the polymeric series. The actual position if it be homogeneous, the average or mean position if it be a mixture.

10. By making use of this process, it is possible to ascertain by an examination of the residual products of a beer or similar liquid, after the primary fermentation is concluded, the values of $[\alpha]$, and κ of the original starch-products as transformed in the mashing process.

11. Although it has been previously shown by one of us that on variously treating the malt-extract prior to saccharification, results are observed indicating a tendency of the reaction to be arrested at certain points corresponding to definite equations; yet, with the exception of No. 8, we have always found, on fractionating such transformations with alcohol, that the dextrin is not homogeneous, but belongs partly to a higher and partly to a lower equation. This is indicated by the differential action of malt-extract on the fractionated dextrans.

12. It follows from No. 11 that the whole of the starch-products in a transformation are not simultaneously affected, but that some portions are hydrolysed faster than others, and that a sharp line of demarcation cannot be drawn between the equations higher than No. 8.

13. The preparation of absolutely non-reducing dextrans is impossible by mere precipitation with alcohol, even when aided by fermentation; but this can be accomplished by treating the dextrin with alkaline mercuric cyanide. This process, unlike the imperfect one of Bondonneau, besides giving the dextrin free from reducing power, allows of its subsequent separation in an *undegraded form*; i.e., it will yield, after treatment with mercuric cyanide, as much maltose when acted on with malt-extract at 60°, as it did before that treatment.

14. The dextrans are not directly fermentable by yeast, but require first to be hydrolysed. Under certain conditions some of the "bottom yeasts," e.g., *Saccharomyces ellipticus* and *S. Pastorianus*, which with other species constitute the secondary ferments of our "high fermentation" beers, are capable of hydrolysing the dextrin for themselves, thus giving rise to an apparent, direct fermentation of that body. That the result, however, is really preceded by hydrolysis is shown by the fact that the dextrans are degraded during the process.

15. When the action of malt-extract on starch-paste is limited, there is always found amongst the products of transformation, besides maltose and dextrin, a *third body* which is more soluble in alcohol than the dextrans, and has a specific rotatory power of $[\alpha]_{D-20} 193.1^\circ$,

and a reducing power of $\kappa_{3.66}21.1$, corresponding to an apparent composition of 34.6 per cent. maltose and 65.4 per cent. dextrin. It is completely hydrated to maltose by the action of malt-extract at 50—60°.

16. This body is doubtless the same as that prepared in an impure state by Herzfeld, and described by him as *maltodextrin*.

17. The following facts prove that maltodextrin is not a mixture of maltose and dextrin:—

- (a.) A mixture of maltose and dextrin prepared so as to have the same optical activity and reducing power as maltodextrin, is separable into its constituents by a single judicious treatment with alcohol.

Maltodextrin is not separable into maltose and dextrin by any possible treatment with alcohol, but is dissolved and precipitated as a homogeneous substance.

- (b.) From a mixture of maltose and dextrin it is possible by means of the *S. cerevisiæ* of the "high fermentation" to ferment the maltose, leaving the dextrin untouched.

Maltodextrin treated in a similar manner is unfermentable.

- (c.) When a mixture of maltose and dextrin is submitted to the action of malt-extract at 50—60° a residue of No. 8 dextrin is always left, the amount being greater the lower in the series the dextrin of the mixture is.

Maltodextrin when acted on by malt-extract under similar conditions is entirely converted into maltose, its amylin constituent leaving no residual dextrin.

18. Whilst maltodextrin is unfermentable by yeast (*S. cerevisiæ* of the high fermentation), it is converted into fermentable, crystallisable maltose by malt-extract, or by the slow action of certain forms of *Saccharomyces* (those accompanying the secondary fermentation) mentioned in the text.

19. We consider that maltodextrin is not, as supposed by Herzfeld, a mere hydration-product of achroodextrin, but that it is produced from starch and the polymeric dextrins by the fixation of a molecule of water upon the ternary group $(C_{12}H_{20}O_{10})_3$, of which there cannot be less than five in the starch molecule, which results in the separation from the dextrin residue of maltodextrin $\left\{ \begin{array}{l} C_{12}H_{22}O_{11} \\ (C_{12}H_{20}O_{10})_3 \end{array} \right.$. This by the fixation of two more molecules of water gives rise to freely fermentable and crystallisable maltose.

LX.—*The Decomposition of Carbonic Acid Gas by the Electric Spark.*

By HAROLD B. DIXON, M.A., The Duke of Bedford's Lecturer on Chemistry at Balliol College, and HUBERT F. LOWE, B.A., late Brakenbury Scholar of Balliol College, Oxford.

THE decomposition of carbonic acid gas by frictional electricity was observed by Landriani and Van Marum; Dalton and Henry repeated the experiment, and examined the gas produced in the decomposition. In 1800, Henry thus describes the effect of the spark on carbonic acid:—

“When the electric shock has been repeatedly passed through a portion of this acid gas, its bulk is enlarged, and a permanent gas is produced which is evidently a mixture of oxygenous and hydrogenous gases; for, when an electric spark is passed through the gas that remains after the absorption of the carbonic acid by caustic alkali, it immediately explodes. These results take place even on electrifying carbonic acid from marble, previously calcined at a low red heat to expel its water, and then distilled in an earthen retort.” (*Phil. Trans*, 1800.)

Buff and Hofmann (*Chem. Soc. J.*, 12, 293) found that an induction spark between platinum wires produced a partial decomposition of carbonic acid, which proceeded rapidly at first and then more slowly, until the liberated carbonic oxide and oxygen combined with an explosion to reform the original volume of carbonic acid.

Berthelot (*Bull. Soc. Chim.* [2], 13, 99) on repeating these experiments found that the decomposition reached no definite limit. On passing the sparks, the volume increased, reached a maximum, and then diminished suddenly but without explosion. When carbonic acid was added to an explosive mixture of carbonic oxide and oxygen, a spark caused explosion and complete combination when the carbonic acid was less than 60 per cent. of the whole, but when the carbonic acid was more than 60 per cent. no explosion occurred, but a series of sparks produced a partial combination which approached no fixed limit.

The experiments of one of us (*Phil. Trans.*, 1884) having shown that no explosion is propagated by a spark in a mixture of carbonic oxide and oxygen dried by standing over anhydrous phosphoric acid, it seemed of interest to repeat the experiments on the decomposition of carbonic acid when dried in a similar manner, and to compare the results with those obtained by the prolonged action of the spark on a dried mixture of carbonic oxide and oxygen. Carbonic acid dried over

anhydrous phosphoric acid was submitted to a series of induction sparks in an eudiometer by means of a chain composed of short pieces of platinum fused into small glass beads, similar to that described by Bunsen. The eudiometer was fitted into the gas analyser described in the paper referred to above. The amount of decomposition varied from time to time, approaching no fixed limit. The maximum decomposition was about 45 per cent., under 100 mm. pressure. Similar results were obtained on introducing a Leyden jar into the circuit of the secondary coil of the Ruhmkorff, but the amount of decomposition was less.

On passing a series of induction sparks through a dried mixture of carbonic oxide and oxygen, partial combination took place gradually, but no fixed limit was reached.

To ascertain what effect a variation in the length of the spark produced on the decomposition, we had an eudiometer made having two pairs of platinum wires, $1\frac{1}{2}$ mm. and 6 mm. apart respectively. This eudiometer was partly filled over mercury with carbonic acid dried by passing through oil of vitriol. Some anhydrous phosphoric acid was introduced into the gas, which was then allowed to stand for several days. The volume when measured and reduced to 0° and 760 was 52.10 c.c. A series of sparks was then passed between the first pair of terminals, $1\frac{1}{2}$ mm. apart, from a Ruhmkorff coil with two Grove cells (1 pint size). The volume gradually increased, and when the coil ceased to act the volume was found to be 62.34 c.c. (reduced to 0° and 760), showing an increase of 10.19 c.c., due to the decomposition of 39.08 per cent. of the original carbonic acid into carbonic oxide and oxygen. The cells were renewed, and the sparks passed continuously for six hours; the volume was then 61.01, showing a decomposition of 33.97 per cent. Three fresh cells were then connected with the Ruhmkorff, and sparks passed between the second pair of terminals (6 mm. aperture) for five hours; the volume was then 60.02, equivalent to a decomposition of 30.20 per cent. Finally one cell alone was used with the smaller aperture (1.5 mm.), and the coil left all night; in the morning it had stopped, and the volume was 63.45, showing a decomposition of 43.33 per cent.

The temperature during the above experiments varied between 10° and 15° , and the pressure was about 500 mm.

These experiments showed considerable variations, but the shorter spark was accompanied by the greater decomposition.

Another set of experiments were made in an eudiometer, with terminals of an alloy of iridium and platinum, the aperture being about 1 mm.

No great variations were observed in this series.

The action of the spark, obtained by inserting a Leyden jar in the

Time from starting.	Volume corrected.	No. of cells.	Temperature. C.	Pressure. mm.	Percentage decomposition.
0 hr.	23·84	—	—	—	—
6 hrs.	27·13	2	12°·0	598	36·0
12 "	26·39	2	14°·0	589	35·8
16 "	26·21	1	12°·8	589	35·4
23 "	26·81	1	13°·2	588	35·7
28 "	26·17	1	13°·6	600	34·8
33 "	25·79	3	15°·0	601	34·4

secondary circuit of the coil, which worked with three cells, was tried between platinum terminals 1 mm. apart.

Time from starting.	Volume corrected.	Temperature. C.	Percentage decomposition.
0 hr.	35·42	—	—
3½ hrs.	41·61	10°·0	34·9
8 "	41·91	10°·5	36·6
11 "	41·92	12°·0	36·7
16 "	39·6	11°·7	23·6
23 "	40·26	13°·5	26·8
25 "	40·23	13°·0	26·7

At the conclusion of this series of experiments, there was a considerable black deposit on the tube, consisting partly, if not entirely, of volatilised platinum, the terminals being at the conclusion of the experiments 0·3 mm. further apart than at the commencement. The widening of the aperture, owing to the volatilisation of the platinum, was accompanied by a decrease in the volume of carbonic acid decomposed.

Another set of experiments was made, using an eudiometer with wires of iridium-platinum alloy 1 mm. apart. Four cells were used, and a Leyden jar inserted in the secondary circuit. Pressure about 500 mm.

Time from starting.	Volume corrected.	Temperature. C.	Percentage decomposition.
0 hr.	25·3	19°·1	—
5 hrs.	29·7	19°·0	34·78
12 "	29·1	19°·5	30·04
18 "	28·5	20°·2	25·30
23 "	28·8	19°·9	27·67

A light black deposit was found in the tube at the conclusion of experiments.

In another series with the same terminals, and with four cells and a Leyden jar, the following volumes were observed.

Time from starting.	Volume corrected.	Percentage decomposition.
0 hr.	16·68	—
7 hrs.	18·88	26·37
15 "	18·56	22·54
22 "	18·31	19·54

The pressure was about 650 mm.

The higher pressure was accompanied by less decomposition.

The variations of volume, which accompanied changes in the nature of the electric discharge, mask the effect of varying pressures in the above experiments. In order to eliminate as far as possible the effect of variations in the spark, a differential process was adopted suggested by Leslie's differential thermometer. Two similar eudiometers were prepared and fitted with wires made of an alloy of platinum and iridium, each wire ending in a sphere about 2 mm. in diameter. These spheres were brought to the same distance apart in the two tubes. On bringing an equal volume of dried carbonic acid into the two tubes, and sending a series of sparks from one Ruhmkorff coil through both tubes at the same time, the gases in the two vessels were found to be equally affected, their volumes varying exactly together so long as the pressure was kept equal in the two tubes. The more feeble the spark, the greater the decomposition of the carbonic acid was found to be. Other conditions being the same, the less the pressure the greater the decomposition of the carbonic acid was found to be.

100 volumes of carbonic acid were introduced into both tubes; in one of them the gas was kept at a pressure of 700 mm. of mercury, and in the other at 500 mm. After an hour, the volumes were measured, and afterwards at intervals of two hours:—

Time from starting.	Volume corrected. Under 500 mm. pressure.	Volume corrected. Under 700 mm. pressure.	Remarks.
—	100·0	100·0	The cells were renewed about four hours from the start.
1 hr.	106·3	103·6	
3 hrs.	119·8	113·7	
5 "	104·3	102·6	
7 "	106·0	104·0	

The gas under the less pressure suffers greater decomposition than the other.

In another experiment, a greater difference of pressure was maintained in the two tubes.

Time from starting.	Volume corrected. Under 250 mm. pressure.	Volume corrected. Under 650 mm. pressure.
0 hr.	100·0	100·0
1 „	105·1	100·9
3 hrs.	104·5	100·8
5 „	103·3	100·4
7 „	112·5	103·3

A greater difference of pressure is accompanied by a greater difference in the percentage of carbonic acid decomposed in the two tubes.

When 100 volumes of dried carbonic acid were brought into one tube, and 150 volumes of a dried mixture of carbonic oxide and oxygen were brought into the other, and a series of sparks were passed through both from the same coil, the volume of carbonic acid increased, and the volume of carbonic oxide and oxygen diminished, until after some hours they became equal under the same pressure. On a further prolonged passage of the spark the two volumes altered together, sometimes increasing and sometimes diminishing, as the nature of the spark varied.

Time from starting.	Carbonic oxide and oxygen. Volume corrected.	Carbonic acid. Volume corrected.
0 hr.	150·0	100·0
1 „	124·6	116·4
3 hrs.	121·5	117·0
5 „	120·5	117·0
7 „	109·3	107·5
9 „	107·3	107·3
11 „	115·6	115·6
14 „	114·3	114·3

A coil of fine platinum wire was heated by a current to whiteness in dried carbonic acid. No permanent alteration of volume was produced. Now Deville has shown that carbonic acid suffers partial decomposition in contact with white-hot platinum. It follows that the dissociated carbonic oxide and oxygen completely reunite under the conditions of the experiment. We were therefore able to predict that a white-hot platinum wire would produce complete combination of dry carbonic oxide and oxygen, even if no explosion occurred in the

mixture. Into the carefully dried eudiometer, standing in the mercury trough, some oxygen was passed, and then two plugs of anhydrous phosphoric acid were introduced into the gas. The platinum wire was then maintained at a white heat for an hour in order that any hydrogen occluded by the metal might be oxidised and absorbed by the drying material. After cooling, the required volume of carbonic oxide, which had been standing for some days over anhydrous phosphoric acid, was introduced, and the mixture was allowed to stand for a week. On heating the platinum wire to redness in the well-dried mixture, it immediately glowed intensely, and after some minutes complete combination was found to have taken place between the two gases. No flame was visible round the glowing wire.

It seems probable that the somewhat abrupt contractions of volume observed by Berthelot in the partially decomposed carbonic acid may have been due to the heating of the platinum wires by the discharge, and the consequent combination of the carbonic oxide and oxygen in the mixture.

The equilibrium observed between the rate of decomposition of carbonic acid and the rate of combination of its products of decomposition appears to differ in one respect from the equilibrium observed in other gaseous systems, such as that studied by Lemoigne between hydrogen and iodine, and the product of their combination, hydric iodide. Whilst hydrogen and iodine probably unite directly together, as hydrogen and chlorine do, carbonic oxide and oxygen require, under the conditions of our experiments, an intermediary to effect their combination. It is uncertain whether the oxidation of the carbonic oxide is brought about in the neighbourhood of the wires by steam molecules still present in the mixture in spite of our process of drying, or by the platinum itself, or in some other way. Possibly, in the course of the spark and in contact with the white-hot metal, some molecules of carbonic oxide are dissociated, and the gaseous carbon is then completely oxidised at one step, as it appears to be in the "explosive wave" formed in the explosion of carbonic oxide and oxygen in a long tube.

LXI.—*The Influence of Silicon on the Properties of Cast Iron.*

By THOMAS TURNER, Assoc. R.S.M. (Demonstrator of Chemistry,
Mason College).

IN order to render our knowledge of the chemistry of iron complete, and at the same time of practical use for everyday application, it is necessary that we should possess accurate information on two points. First, a ready and correct method for the estimation of the amount of each constituent, and, secondly, a knowledge of the exact influence on the character of the product, which is exerted by different quantities of each element present. During recent years much has been done in these two directions, but, so far as I am aware, hitherto little advance has been made towards the determination of the influence of silicon on the properties of iron and steel.

Dr. Percy, writing twenty-one years ago, said, "There is no element of which it is more important to study the action in relation to the smelting and manufacture of iron than silicon; and yet our knowledge of this action is still very imperfect" (*"Metallurgy of Iron and Steel,"* p. 80). And, even now, one cannot read our best text-books without noticing the very divergent statements which are made on this subject, and without regretting the frequent absence of experimental evidence for the statements made.

Mr. I. Lowthian Bell, one of our best known and most trustworthy authorities on matters connected with the chemistry of iron, says: "With regard to the influence of silicon on the quality of pig-iron, it may be questioned whether it is ever beneficial. Even in moderate quantities, the metal is undoubtedly rendered weak as a material for the purposes of the founders, and its presence in any quantity in forge iron is undoubtedly detrimental" (*"Chemical Phenomena of Iron Smelting,"* 1872, p. 286). "Iron containing any approach to 6 or 7 per cent. of silicon is absolutely useless in the foundry and forge. It is extremely brittle when in the form of castings, and its richness in silicon renders it perfectly unmanageable, either in the refining or puddling furnace, owing to its powerful action on the masonry. . . . Silicon is useful in increasing the fluidity of the metal, and, in consequence, ought to be sought after, in moderate quantities, for fine castings. Where strength is required it is prejudicial, and in the puddling furnace its presence is the reverse of desirable, for it not only diminishes the yield by its presence, but it increases the waste" (*"Manufacture of Iron and Steel,"* 1884, p. 162).

The statements just quoted probably give the best and most accurate account of the present state of our knowledge on this subject,

and authorities appear to agree in stating that any addition of silicon to cast iron must be prejudicial to its strength. The following experiments were commenced with the intention, if possible, of determining the extent of this influence by a suitable series of mechanical tests. They lead to the conclusion that, at all events under the circumstances given, a suitable addition of silicon to cast iron may considerably increase its tenacity.

The general plan of work was to prepare cast iron, containing different, though definite, amounts of silicon, 0, 1, 2, 3, 4, &c., per cent. From this metal, test bars were to be prepared, and, after mechanical testing, to be chemically analysed, so as to check their composition. The method adopted was as follows: "pure cast iron" was prepared, as afterwards described, and mixed, by melting in crucibles, with the necessary amount of silicon pig-iron containing about 10 per cent. of silicon. It was found practicable by this simple method to add to the iron the exact quantity of silicon required, the error usually not exceeding one-twentieth per cent. It may be well to explain that the term "pure cast iron" is applied to a metal which should contain pure iron, together with at least 2 per cent. of carbon, and the smallest possible quantity of any other element.

This "pure cast iron" was prepared by a method which was rendered troublesome by the fact that my furnace could only take a crucible 6 inches broad by, at most, 9 inches high. About 4 kilos. of South Staffordshire $\frac{1}{2}$ -inch round iron, in $4\frac{1}{2}$ -inch lengths, was placed in a Stourbridge clay crucible, which was afterwards filled up with powdered charcoal. The crucible was then covered, placed on a brick in the furnace, and heated by coke to the highest attainable temperature for about five hours. At the end of three hours, it was usually found that the wrought iron had completely melted, and, by stopping the action at this stage, a steel containing about 1.5 per cent. of carbon was obtained. By continuing the heat for a longer period, 3 per cent. of carbon could be introduced, and probably more could have been added, although that is the highest amount reached in these experiments. For reasons which will be explained later, it was considered expedient to have 2 per cent. of carbon present, and this could be obtained by keeping the metal fluid, with occasional stirring, in contact with powdered charcoal, for a period of two hours. The metal was then cast into ingots in sand, and the ingots were broken up into about six pieces, each as nearly as possible of the same size. Pieces were taken each from a different ingot in the remelting, so as to secure greater uniformity of composition. By this means a cast iron was obtained exceptionally low in all the impurities which are found in the commercial article; silicon never exceeded 0.2 per cent., whilst the amount of carbon present had been previously

determined upon, and never varied more than ± 0.23 per cent. from the desired amount.

The silicon pig-iron employed has already been mentioned in a recent paper (this vol., p. 474), its composition being—

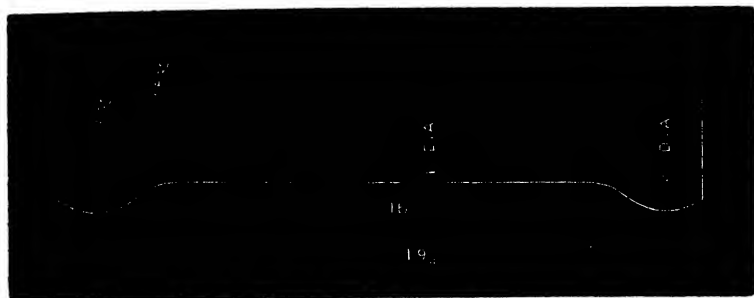
Total carbon	1.81
Graphite	1.12
Silicon	9.80
Manganese	1.95
Phosphorus	0.21
Sulphur	0.04

It will be noticed that the percentage of carbon is low for a pig-iron, and attempts were made to increase this amount by heating the metal for some hours in contact with charcoal, as in the preparation of pure cast iron. But it was not found possible, even by prolonged action, to alter the amount of carbon more than a few tenths per cent., and the characteristic appearance of the metal remained unaltered. Thus it became apparent that at one end of the series iron must, of necessity, be employed, which would contain about 2 per cent. of carbon, and that was one of the chief reasons which led to the adoption of a 2 per cent. carbon series. It is obvious that if it is desired to study the effect of any one constituent, all the other substances must be kept as nearly constant as possible. Among other reasons was the fact that with 2 per cent. of carbon we have the lower limits of cast iron, and, when other constituents are present in small quantity, the real effect of the addition of silicon might reasonably be expected to be more apparent. It may be added that the ingots of "pure cast iron" were submitted to the inspection of men with large practical experience in the iron trade, who, from the fracture and general appearance, pronounced the metal to be "white iron of superior quality."

A supply of metal suitable for the purpose in hand having thus been obtained, the test bars were prepared as follows. About 4 kilos. of metal, containing the necessary proportions of pure cast iron and silicon pig was melted in a Stourbridge clay crucible, in which about 10 grams of charcoal had previously been placed, with the object of just counteracting the effect of oxidation during melting. When the iron was thoroughly fluid and ready to pour, it was well stirred by means of an iron rod, and immediately cast into an upright purpose of mould, arranged so as to leave a good sized head, for the purpose of ensuring a sound casting. Fig. 1 is taken from a sketch which the test me by Professor A. B. W. Kennedy for the pattern from which the test pieces were cast. In each case, the test bars were allowed to remain about 15 hours in the mould before being removed," so as to avoid

the ill effects of chilling; they were then roughly dressed, and tested with the skin on, the size being fairly uniform.

FIG. 1.—Sketch for Cast-iron Specimen (pattern).



Through the kindness of Professor Kennedy, the mechanical tests were performed by the well-known University College testing machine, and I would here express my deep indebtedness to him for the very important part of the work which he has performed.

In the following table (A), a summary of the results of tensile tests is given; in the second column are numbers giving the percentages of silicon which it was intended to introduce. In Table B is given the exact composition as determined by analysis, from which it will be found that the total carbon, sulphur, and phosphorus are very nearly constant, the silicon agrees very nearly with that intended, whilst the manganese gradually increases to a maximum of 1·95 per cent.

TABLE A.—*Summary of Tensile Tests* (by Professor Kennedy).

U. C. L. test numbers.	Silicon per cent.	Breaking load per square in.		Modulus of elasticity.
		Pounds.	Tons.	
8807	0	22,720	10·14	25,790,000
8448	0·5	27,580	12·31	28,670,000
8447	1	28,490	12·72	31,180,000
8446	2	35,180	15·70	23,560,000
7867	2·5	32,760	14·62	25,450,000
8445	3	27,390	12·23	21,150,000
8444	4	25,280	11·28	15,640,000
8894	5	22,750	10·16	18,720,000
7866	7·5	11,950	5·34	14,750,000
7865	10	10,630	4·75	13,930,000

TABLE B.—*Results of Analyses* (by T. Turner and J. P. Walton).

U. C. L. test numbers.	Total carbon.	Graphite	"Com- bined" carbon.	Silicon.	Phos- phorus.	Manga- nese.	Sul- phur.
8807	1·98	0·38	1·60	0·19	0·32	0·14	0·05
8448	2·00	0·10	1·90	0·45	0·33	0·21	0·05
8447	2·09	0·24	1·85	0·96	0·33	0·26	0·04
8446	2·18	1·62	0·56	1·96	0·28	0·60	0·03
7867	1·87	1·19	0·68	2·51	0·26	0·75	0·05
8445	2·23	1·43	0·80	2·96	0·34	0·70	0·04
8444	2·01	1·81	0·20	3·92	0·33	0·84	0·03
8894	2·03	1·66	0·37	4·74	0·30	0·95	0·05
7866	1·86	1·48	0·38	7·33	0·29	1·36	0·08
7865	1·81	1·12	0·69	9·80	0·21	1·95	0·04

Fig. 2 (p. 582) is a curve which represents graphically the effect of the introduction of silicon into "pure cast iron," as measured by differences in tensile strength of the product.

The following remarks were appended to his report by Professor Kennedy, and it is thought well to record them here:—

8807. Crystalline, silvery, not sound, round edges.

8448. Silvery, a blowhole about $\frac{1}{4}$ " diameter.

8447. Silvery, with some large facets, irregular and discolored in centre, somewhat unsound.

8446. Close grained, blue-grey, somewhat unsound and lighter in colour than 8444.

7867. Sound, only one small blowhole, broke close to head beyond smallest part of piece; appearance that of ordinary close grained cast iron.

8445. Similar to 8446.

8444. Close grained, blue-grey, somewhat unsound.

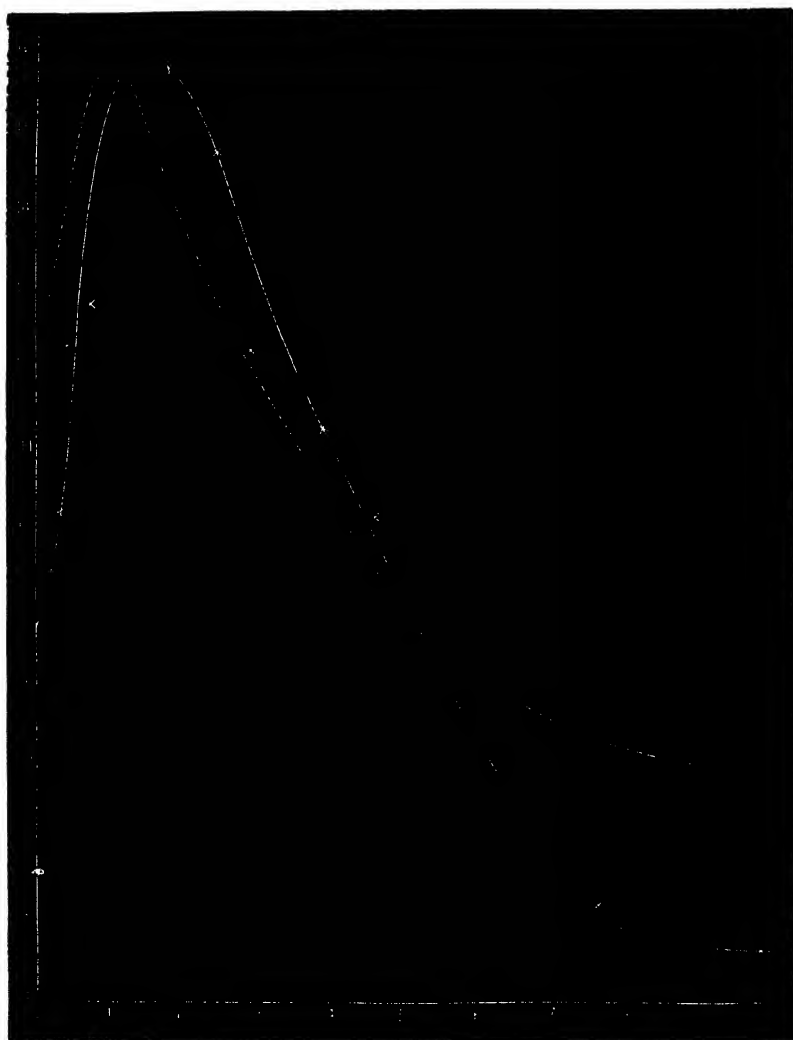
8894. Close grained, grey (somewhat dark), granular fracture, slight trace of unsoundness.

7866. Sound, close grained, silvery fracture without any large facets, colour resembling 8894, but not so white; broke in middle.

7865. Large crystalline, with silvery facets, colour very light. Broke through head of piece where casting was very unsound.

It may be added that, with the exception of 7865, and to which subsequent reference will be made, all the test-bars were considered to be fairly representative specimens, and such as would be accepted for practical purposes. The unsoundness noticed was generally very

Fig. 2.—Effect of Silicon on Cast Iron. Tensile Strain and Modulus of Elasticity.



Silicon per cent.

× Experimental points Tensile Strain.

○ Experimental points Modulus of Elasticity.

slight, and occurs with the stronger specimens as much as, or more than, with the weaker. In cases where any doubt existed, fresh specimens were prepared.

It is to be regretted that in the foregoing experiments it was not possible to keep the amount of manganese as constant as in the case of the other constituents; this fact naturally introduces a slight uncertainty as to how much of the effect noticed is really due to silicon alone. It must be borne in mind, however, that this error cannot be very great, not only from the known characters of alloys of manganese with iron, but because the amount of silicon introduced was in every case five times as great as that of the manganese simultaneously added. Hence it may reasonably be assumed that the effect observed is due almost entirely to silicon, and that a suitable addition of silicon to pure cast iron may considerably increase its tensile strength. Of course, any further addition beyond this point very much deteriorates the quality of the iron. We should expect, from analogy, when the amount of other constituents is large, that the suitable proportion of silicon would be diminished, and it will be found that our most esteemed qualities of pig iron all contain some silicon, though they seldom or never exceed the allowable limit, of 2.5 per cent., which may be deduced from our experiments. It may reasonably be questioned from these experiments whether, in all cases where strength is required, it would not be found best to introduce between 1 and 2 per cent. of silicon.

In connection with the modulus of elasticity, results are obtained which it is rather difficult to satisfactorily explain. The "modulus of elasticity" represents a theoretical conception, and is the number of pounds per square inch which would be required to double the length of the specimen, if elongation continued throughout as observed in the experiment. For wrought iron and steel, this number is generally about 30 millions, whilst for cast iron it is about half that amount. It will be noticed that the modulus is not very uniform, although it shows two remarkable features. In the absence of silicon, it is about double what is generally observed, and further, this increases on addition of a little silicon, and diminishes again on continuing that addition.

The high initial modulus may probably be accounted for by the fact that the iron is only just past the steely range, and so, while possessing some of the properties of cast iron, it also possesses some of the characters of steel. This would account for its greater hardness and high modulus. And, since silicon is generally regarded as acting in a manner very similar to that of carbon, though in a smaller degree, we are able to account for the modulus being lowered by the addition of much silicon. But at present I must confess that I am not prepared with an explanation, on this principle, for the *increase* in the modulus on the addition of a moderate amount of silicon. It does, however, show that the metal is improved by the addition of a

small quantity of silicon. This may possibly be due, as has been suggested in other cases, to a certain neutralising or masking effect which definite quantities of certain impurities exert upon each other.

In Fig. 2, the dotted line gives the most probable direction of the modulus of elasticity curve. It will be noticed that in three cases the experimental results do not agree well with the curve; there can, however, be little doubt but that the general shape of the curve is correct, and it is seen to be of the same general form as the curve of tensile strain.

Some account of the other physical properties of the different specimens may be of value. It has been noticed by many observers that silicon renders iron more fluid, and reference to this fact will be found in the remarks of I. Lowthian Bell which have been previously quoted. This effect appears to be regular and progressive, and is very marked during pouring and casting. Silicon pig when melted is perfectly limpid and clear; it pours like water, fills all the vent-holes with fine needles of metal, and spreads itself in a thin sheet along all the joints of the mould. Pure cast iron is comparatively viscid, does not penetrate the vent-holes and joints, and gives a rougher casting, while silicon pig has a beautifully smooth skin. In quantities of from 2 to 5 per cent. the addition of silicon undoubtedly rendered the metal more sound; below that lower limit the metal often contained round blowholes with a dark and roughened interior. But it is noticeable that silicon pig itself was very difficult to cast sound in quantity. In this case during solidification a long hollow runner would often form inside, and no amount of "feeding" during solidification would entirely prevent this. Its effect is noticed in the faulty head of the test-bar. In almost every case only *one* long hole was formed, which was smooth and glazed inside, and there was always sound metal above. Hence it appears possible that the effect of silicon in rendering castings more sound may be partly physical. Pure cast iron tends to become porous, or to "blow out" during solidification, whilst silicon pig shows a marked contraction. By suitable mixtures, the one tendency can be made to neutralise the other, and a sound casting is produced. But, of course, such a physical action would be but a part of the influence exerted by silicon, as probably when small quantities are added, for steel castings, the effect is almost entirely chemical.

In connection with resistance to shock, I have not been able as yet to make any quantitative determinations with different percentages of silicon. Some rough observations have, however, been made in breaking bars by means of a blow from a hammer. Metal containing 1 and 2 per cent. of silicon broke with great difficulty, and only after

being struck several times with full force. Metal with 0, $\frac{1}{2}$, and $2\frac{1}{2}$ per cent. was very strong but broke rather more easily than the first mentioned; still the difference was not marked. With 3 and 4 per cent. the metal was still good though not so strong; with 5 per cent. the metal was rather weak, with $7\frac{1}{2}$ per cent. the weakness was more marked, while with 10 per cent. a bar could be broken at any desired place by a moderate blow, and the fragments readily crushed in an iron mortar. Such comparisons are of little value, except, perhaps, to the observer himself, but the opinion formed was, that no sensible deterioration resulted until upwards of 2 per cent. of silicon had been added.

Dr. Percy ("Metallurgy of Iron and Steel," p. 131) has referred to the fact, which he states was first noticed by Sefström, that in cast iron which contains much silicon, the carbon occurs chiefly in the graphitic state. This is illustrated in the table of results of analyses previously given, from which the following figures are taken:—

Silicon.	Total carbon.	Graphite.
0.45	2.00	0.10
0.96	2.09	0.24
1.96	2.18	1.62
2.96	2.23	1.43
3.92	2.01	1.81

In each case, the conditions of cooling were as nearly as possible the same, so the effect noticed must depend on the composition of the metal. The fact that this result is not so marked in silicon pig itself is probably due to the presence of manganese, which acts in a contrary manner.

Some reference has previously been made to the appearance on fracture. This in the pure cast iron was white, becoming more silvery with $\frac{1}{2}$ and 1 per cent. of silicon. At 2 per cent. it was grey, becoming gradually darker in colour up to 5 per cent.; at $7\frac{1}{2}$ per cent. it was again lighter, and slightly glazed, whilst the fracture of the silicon pig itself may be best described (in the words of Dr. Percy used in reference to small buttons of similar composition obtained in one of his experiments) as "light grey, highly crystalline, and presenting aggregations of minute bright faces set at various angles, so that, on varying the direction of the incident light, every part appeared bright in succession, although in any one position the fracture appeared to consist of about an equal proportion of dull and grey parts."

We cannot leave this part of the subject without referring to a familiar kind of iron, formed with certain known conditions of working in the blast furnace, and which, from its peculiar appearance, is

called "glazed pig" or "burnt iron." This variety of metal is known to be of very little value for the foundry or forge, being too rotten for castings, and too fluid for puddling. Its peculiar characters are known to be connected with the high percentage of silicon present, and on several occasions I have been able to judge with considerable accuracy of the percentage of silicon, simply by the appearance on fracture. But the "glazed" character would appear to be influenced by circumstances other than the mere silicon content. Thus, in the following analyses, we find the glazed appearance is by no means dependent upon the percentage of silicon alone, but also upon some other factor which from lack of sufficient information I am not able to explain.

Kind of iron.	Silicon.	Character
South Staffordshire	4·33	No. 1, grey.
" " " " " " " " " " " "	4·72	Glazed.
Test bar 8894.....	4·74	Close grained dark grey, granular.
South Staffordshire	5·39	No. 1, grey. [lar.]
Test bar 7866	7·33	Grey, slightly glazed.

Here the work must be left for the present, but I hope shortly to be able to bring before the Society some fresh facts, together with a short summary of the conclusions deduced from the whole of these experiments.

I would again gratefully acknowledge the help received from my friend Mr. J. P. Walton, Assoc. R.S.M., who has rendered important assistance in the analytical work recorded in this paper.

LXII.—*Brominated Derivatives of Diphenyl, Tolybenzene, and Ditolyl.*

By THOMAS CARNELLEY, D.Sc., and ANDREW THOMSON, M.A., B.Sc.,
University College, Dundee.

THE hydrocarbons used in the following investigation were obtained by passing the mixed vapours of benzene and toluene through a red-hot tube, according to the method described by one of us (this Journal, 37, 701).

1. The diphenyl, $C_6H_5 \cdot C_6H_5$, after recrystallisation from alcohol, melted at 70° and boiled at $245-258^\circ$.

2. The 1.4 tolylbenzene, $C_6H_5 \cdot C_6H_4 \cdot CH_3$, was a colourless liquid boiling at $263-268^\circ$, and on oxidation gave first 1.4 phenylbenzoic acid melting at $216-220^\circ$, and finally terephthalic acid.

3. The 1.2 : 1'.4' ditolyl, $CH_3 \cdot C_6H_4 \cdot C_6H_4 \cdot CH_3$, was a liquid boiling at $272-280^\circ$, and on oxidation gave, first 1.2 : 1'.4' tolylbenzoic acid, $CH_3 \cdot C_6H_4 \cdot C_6H_4 \cdot COOH$, melting at $179-180^\circ$, and finally terephthalic acid.

I. Derivatives of Diphenyl.

Tribromodiphenyl, $C_6H_4Br \cdot C_6H_3Br_2 = 1.4 : 1'. ? ?$. No tribromoderivative of diphenyl has been previously described. The above compound was obtained accidentally by the action of bromine on a mixture of diphenyl with 1.4 tolylbenzene: 5 grams of the mixed hydrocarbons boiling at $256-264^\circ$ were treated with excess of bromine; the product after standing several hours was freed from excess of bromine by repeated shaking with caustic soda, and finally well washed with water. From the crude substance thus obtained, the tribromodiphenyl was separated by frequent extraction with alcohol in which it was scarcely soluble; after purification by recrystallisation from a large quantity of alcohol, it was finally obtained in colourless silky needles. It melts at 90° , and is very sparingly soluble in alcohol, even when hot, and is non-volatile in steam. It gave the following results on analysis:—

	Calculated.	Found.
$C_{12}H_7Br_3$	61.38	61.77 per cent. Br.

On oxidation with chromic and glacial acetic acids, it gave 1.4 bromobenzoic acid melting at 248° . Hübner and Retchy (*Zeit. Chem.* [2], 7, 631) give 251° as the melting point of this acid, a result also confirmed by other observers. Hübner, however (*Ber.*, 10, 1704), gives $248-251^\circ$, whilst Hübner and Post (*Annalen*, 169, 1) give 245° .

Dibromodiphenyl, $BrC_6H_4 \cdot C_6H_4Br = 1.4 : 1'.4'$. Having obtained tribromodiphenyl as above described, we then attempted to obtain the same compound by the action of excess of bromine on *pure* diphenyl. Though we were unable to prepare the compound in this way, the results were nevertheless interesting in so far as the experiments gave rise to two different crystalline modifications of dipara-dibromodiphenyl. 5 grams of pure diphenyl were dissolved in 15 grams of carbon disulphide, and 16 grams of bromine gradually added to the mixture, a violent reaction then took place, though the liquid was well cooled. When the action had entirely ceased, the product was digested on a water-bath with a reversed condenser for two days, 1 gram of bromine was then added, and the whole heated in a sealed

tube for two hours at 90°. On cooling, the carbon disulphide was distilled off, and the last traces of bromine removed by caustic soda. After well washing with water, the product was treated with hot alcohol, in which it was for the most part insoluble. The insoluble residue, on crystallisation from carbon disulphide, gave a crop of crystals which were of two kinds, (a) prisms, and (b) octohedra. These were separated mechanically. (a.) *The prisms*, when recrystallised from carbon disulphide, were quite free from octohedra, and were drained, washed with hot alcohol, and dried. They melted at 162°, and consisted of brilliant, colourless, highly refractive prisms. They were almost entirely insoluble in alcohol, and only moderately soluble in carbon disulphide and cold benzene. A portion recrystallised from benzene gave the following results on analysis:—

	Calculated.	Found.
$C_{12}H_8Br_2$	51.28	51.40 per cent. Br.

(b.) *Octohedra*. These, after being picked out from the prisms, were washed with a mixture of alcohol and ether to remove any traces of the prismatic modification, which was more soluble therein. After drying they melted at 162°. Many of the crystals were perfect octohedra. They were insoluble in cold, and nearly insoluble in hot alcohol. They were but little soluble in a mixture of alcohol and ether.

On analysis they gave the following results:—

	Calculated	Found.
$C_{12}H_8Br_2$	51.28	51.20 per cent. Br

These results show that both prisms and octohedra consisted of dipara-dibromodiphenyl.

Fittig (*Annalen*, 132, 204) and Strasse and Schultz (*ibid*, 210, 191) give the melting point of this compound as 164°.

* It thus appears that dipara-dibromodiphenyl exists in two modifications crystallising in different forms, the one in prisms and the other in octohedra. Of these, the latter does not appear to have been previously observed, for all published accounts describe dipara-dibromodiphenyl as crystallising in large colourless prisms having a splendid lustre, and a strongly refractive power. Dibromodiphenyl appears to be slightly volatile in steam.

II. Derivatives of Tolyllbenzene.

Monobromo 1.4 tolyllbenzene, $C_{13}H_{11}Br$.—This compound was prepared by brominating the hydrocarbon (b. p. 263–267°) obtained by the action of sodium on mixed monobromobenzene and 1.4 mono-

bromotoluene. The bromine was added until solidification set in, excess of bromine being removed as usual by caustic soda. The product was washed with water and extracted with cold alcohol. The residue after several recrystallisations from hot alcohol yielded small pearly plates, which melted at 131° . The compound is almost insoluble in cold and only sparingly soluble in hot alcohol, but is very easily soluble in benzene. The same compound was prepared by the action of the calculated quantity of bromine on the 1.4 tolylbenzene, obtained by the action of heat on the mixed vapours of benzene and toluene. It crystallised in small pearly plates melting at 127 – 129° , exactly resembling those obtained by the first method.

An analysis of the first preparation gave—

	Calculated.	Found.
$C_{13}H_{11}Br$	32.39	32.03 per cent. Br.

Dibromotolylbenzene, $C_{13}H_7Br_2 \cdot CH_3$.—Two isomeric modifications of the above formula were obtained by the action of bromine upon 1.4 tolylbenzene, but it was not found possible to separate them.

Dibromophenylbenzoic acids, $C_{13}H_7Br_2 \cdot COOH$.—Two of these acids were obtained by the oxidation of the mixed dibromo 1.4 tolylbenzenes referred to above. For this purpose the mixed bromo-compounds were oxidised with a deficit of chromic and glacial acetic acids, the liquid boiled for an hour, precipitated by admixture with a large quantity of water, and filtered. The precipitate, after digesting with warm ammonia, was filtered from the residue (A). The filtrate on acidification with hydrochloric acid gave a white curdy precipitate, which was redissolved in ammonia, in which it was nearly all soluble, and again precipitated by hydrochloric acid. The precipitate was finally purified by being twice recrystallised from alcohol and sublimed. It melted at 201.5° to 203.5° , and resolidified at 200 – 201° . It sublimed in small needle-shaped prisms, which were not very soluble in alcohol.

Analysis gave as follows :—

	Calculated.	Found.
$C_{13}H_5Br_2O_2$	44.94	45.20 per cent. Br.

The residue (A) mentioned above was reoxidised with chromic and glacial acetic acids, the solution precipitated by water, and the precipitated acid, after being collected and washed, was treated with ammonia, in which it was almost completely soluble. It was reprecipitated by acidification with hydrochloric acid. After washing and drying, it melted at 232° . When heated on a watch-glass, it sublimed easily and almost completely without melting. After sublimation, it melted at 232° , and resolidified above 225° . On re-fusion, it melted at 231° .

Analysis gave—

	Calculated.	Found.
$C_{11}H_8Br_2O_2 \dots$	44.94	45.46 per cent. Br.

The production of these two acids shows that the dibromo 1.4 tolylbenzene obtained by the action of bromine on the hydrocarbon is a mixture of two modifications, of which the one is more easily oxidised than the other, giving the corresponding dibromophenylbenzoic acids, melting at 202° and 232° respectively.

III. Ditolyl.

Monobromoditolyl, $C_6H_4Me \cdot C_6H_3BrMe = 1.2 : 1' : (2' \text{ or } 3') : 4'$.

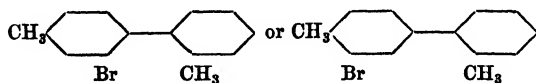
7.125 grams of 1.2 : 1'.4' ditolyl were treated gradually with an equivalent quantity of bromine, the whole being kept cool. After the somewhat violent action had ceased, the excess of bromine was removed as usual with caustic soda. The product was dissolved in a large quantity of alcohol from which on cooling a brown oil separated, followed by a large crop of crystals. The crystals were separated from the oil (B), and recrystallised five times from alcohol. The melting point was then constant at 93—95° (corr.). The compound crystallises in fine interlacing microscopic needles, which are only very slightly soluble in cold alcohol, and sparingly soluble in hot, but easily soluble in ether or benzene.

Analysis gave :—

	Calculated.	Found.
$C_{14}H_{13}Br \dots \dots$	30.65	30.94 per cent. Br.

On oxidation with chromic and glacial acetic acids, it gave an acid melting at 290—295° (uncorr.) = 304—309° (corr.) and slightly soluble in benzene.

³Monobromoterephthalic acid melts at 304—305° (Fischli, *Ber.*, 12, 619). This shows that the constitution of the monobromoditolyl is—



Monobromoditolyl, $C_6H_4Me \cdot C_6H_3BrMe = 1.4 : 1' : 4' : 2'$.—The oil (B) referred to above, after removal of the whole of the crystalline monobromoditolyl, was thoroughly dried and analysed :—

	Calculated.	Found.	
		(1)	(2)
$C_{14}H_{13}Br \dots \dots$	30.65	30.24	30.70 per cent. Br.

On oxidation it gave (1) monobromodiphenic acid and (2) monobromophthalic acid as under.

Monobromodiphenic acid, $C_6H_4(COOH) \cdot C_6H_3Br \cdot COOH$, 1.4 : 1'.4'.2'.—For the preparation of this acid, 0.850 gram of the liquid monobromoditolyl was oxidised with the calculated quantity of chromic and glacial acetic acids, and the acid precipitated from the resulting liquid by excess of water. It was redissolved in ammonia and reprecipitated by hydrochloric acid. After drying it melted at 208° (uncorr.) = 215° (corr.), and on analysis gave—

	Calculated.	Found.
$C_{14}H_9BrO_4$	24.92	23.88 per cent. Br.

The further purification and another analysis were impossible, owing to the small quantity of material at our disposal. That its constitution was such as is represented above was shown by that of the following acid :—

Monobromophthalic acid, $C_6H_3Br(COOH)_2$ = 4.2.1.—This acid was obtained by oxidising 1.2 gram of liquid bromoditolyl with 10 grams of chromic acid dissolved in glacial acetic acid. It melted at 197° (uncorr.) = 203° (corr.), and after drying at 105° gave the following result on analysis :—

	Calculated.	Found.
$C_8H_5BrO_4$	32.65	32.20 per cent. Br.

That this acid is parabromophthalic acid is shown by its melting point, for in the original liquid bromoditolyl, the bromine must be in the nucleus in which the methyl is in the ortho-position, otherwise bromoterephthalic acid would have been obtained on oxidation. Now only two bromophthalic acids are possible, viz., $C_6H_3Br(COOH)_2$ = 4.2.1 and 3.2.1, and the latter of these melts at 138 – 140° as shown by v. Pechmann (*Ber.*, 12, 2126), consequently the one we have obtained must be the 4.2.1 compound; an acid of this constitution seems to have been also obtained by v. Pechmann along with the 3.2.1 acid, but he was unable to obtain it in an isolated state.

Dibromoditolyl, $C_{14}H_{12}Br_2$.—7.77 grams of ditolyl dissolved in carbon disulphide were treated with the calculated quantity (12.4 grams) of bromine, the liquid being kept cool. After removing excess of bromine with caustic soda, the product was boiled with a large quantity of alcohol from which a great portion crystallised out on standing. The mother-liquor contained chiefly the above liquid modification of monobromoditolyl. The crystals after being twice recrystallised from alcohol melted at exactly 152° (uncorr.) = 156° (corr.). This compound crystallises in beautiful, long, almost hair-fine, needles of brilliant lustre. They are much less soluble in alcohol than either of

the monobromo-compounds. The solution in alcohol when allowed to crystallise under the microscope was found to yield two sets of crystals:—(1) The great bulk consisted of rosettes of slender needles, (2) a very small quantity of minute perfect octohedra. Both varieties of crystals seemed equally soluble in alcohol, and we were consequently unable to separate them.

Analysis gave :—

	Calculated.	Found.
$C_{14}H_{12}Br_2$	47.06	47.42 per cent. Br.

This dibromo-compound behaves in a remarkable manner on oxidation. A portion was oxidised with a quantity of chromic and glacial acetic acids, sufficient for complete oxidation, *i.e.*, to yield one of the phthalic, or one of the bromophthalic acids, and the liquid boiled for half an hour. On pouring the product into cold water, a thick bright yellow precipitate was obtained, which after washing well with hot water, and drying, melted at 166° (uncorr.) = 170° (corr.). This compound did not appear to be an acid, for it was quite insoluble in hot ammonia, caustic soda, or caustic potash, but dissolved in alcohol to a bright yellow liquid.

On analysis it gave :—

	Calculated.	Found.
$C_{14}H_8Br_2O_2$	43.71	43.70 per cent. Br.

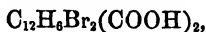
Another preparation made in exactly the same way gave as melting point 170° (corr.), and was in all respects similar.

A portion of this compound was boiled with a large excess of chromic and glacial acetic acids for more than an hour. On diluting with water, a thick yellow precipitate was obtained as previously. It was well washed with hot water, and after drying melted at 197 — 198° (uncorr.) = 201 — 202° (corr.). Like the previous compound, it was insoluble in hot ammonia, caustic soda, or caustic potash, but soluble in hot alcohol to a bright yellow liquid, from which it crystallised in minute yellow needles. It was also easily soluble in cold benzene and cold ether to an intensely yellow liquid. To all appearance it seemed identical with the compound previously obtained and melting at 170° , but its real difference was shown both by its melting point (201 — 202°) and by its composition, which was as follows :—

	Calculated.	Found.
$\left\{ \begin{array}{l} C_{14}H_8Br_2O_4 \dots \dots \dots \\ C_{14}H_8Br_2O_4 \dots \dots \dots \end{array} \right.$	$\begin{array}{l} 40.20 \\ 40.00 \end{array}$	39.82 per cent. Br.

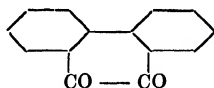
The same compound melting at exactly the same temperature was also obtained directly when the dibromoditolyl was oxidised with excess of chromic and glacial acetic acids.

What the constitution of these bodies really is, we are at present unable to say with certainty. The one melting at 201° contains the percentage of bromine required for dibromodiphenic acid,

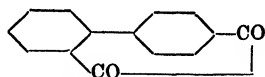


but its acid character seems to be negatived by its insolubility in caustic alkali.

The compound melting at 170° has the composition of a double ketone, $\text{C}_{12}\text{H}_6\text{Br}_2 : (\text{CO})_2$, and is, therefore, isomeric with dibromophenanthraquinone, m. p. 230° (*Annalen*, **167**, 185).



Phenanthraquinone.



Quinone from which our dibromo-compound, $\text{C}_{12}\text{H}_6\text{Br}_2 : (\text{CO})_2$, m. p. 170° , is derived.

This is an example of the unusual formation of a diketone, in which the two CO-groups are not both in the ortho-position.

We are still engaged with these two compounds, and also in the preparation of other derivatives of these hydrocarbons.

LXIII.—On the Cause of the Decrepitations in Samples of so-called Explosive Pyrites.

By B. BLOUNT.

DURING the latter part of 1884, a sample of copper pyrites came into my hands from the Cosheen Copper Mine on Scull Harbour, County Cork. The ore is remarkable on account of its richness, as is shown both by the analysis which is appended to this paper, and by the report of the Swansea assayers, to whom a specimen was sent. But the most noteworthy characteristic in this specimen was its property of exploding, or decrepitating violently, when gently heated. This singular behaviour seemed worthy of investigation, especially as certain cargoes of iron pyrites are rejected by the vitriol makers on this account; to the best of my knowledge no cause has been assigned for such behaviour.

Through the kindness of Professor Huntington of the Metallurgical Department of King's College, two samples from such cargoes have been placed at my disposal, but the work done has been

almost exclusively on the Irish copper ore, as it explodes at a far lower temperature, and was therefore easier to deal with than the others, although it appears probable that their decrepitations are analogous in character, and differ only in degree.

All the experiments, except where expressly stated to the contrary, were made with the copper pyrites.

The appearance and sp. gr. of the pyrites was similar to that of the ordinary ore; it broke readily under the pestle, with a decided tendency to do so in planes, and was easily reduced to fine powder; as stated above, it decrepitated readily and with violence when gently heated, doing so even under hot water. Exsiccation over sulphuric acid in no wise diminished its explosive power, but when roughly powdered it was found that the decrepitations became feebler, and ceased altogether, if it was tolerably finely powdered.

Three hypotheses may be advanced to account for the phenomenon. That the decrepitations were produced by—

(1.) The expansive force of water contained in cavities in the interior of the ore.

(2.) The expansive force of a gas, similarly imprisoned, and probably at a high pressure.

(3.) The movements of molecules in a state of tension in their efforts to attain equilibrium.

Experiments were instituted with regard to the first and second. A weighed quantity of the pyrites was decrepitated in a Liebig's tube by heating it at 100° , and any evolved gas or water vapour led into weighed absorption tubes. By this means, it was shown that a gas was evolved during the heating, which was completely absorbed by caustic potash, and unabsorbed by strong sulphuric acid. It is noteworthy that the first decrepitation took place at 24° , and one piece resisted the disintegrating force till 95° had been reached.

The small sample first sent was soon exhausted, and after waiting some weeks a second and larger portion was obtained, but somewhat inferior in appearance and vigour of explosion to the first. This second lot, on being decrepitated under like conditions, evolved not only a gas absorbable by potash but also a little water.

Barium hydrate was now substituted for the potash, the absorption taking place as before, with the addition of the formation of a white precipitate, which was soluble with effervescence in dilute acids, did not liberate iodine from iodic acid, nor decolorise weak acid permanganate. It was therefore concluded that the gas was carbonic anhydride. The numerical results of one of these determinations is appended.

Weight of pyrites taken.....	13.1515	grams
Loss on heating	0.0167	„
Gain of Ba(OH) ₂	0.0100	„ (CO ₂)
„ H ₂ SO ₄	0.0052	„ (H ₂ O)
	<hr/>	
Total gain.....	0.0152	„

Difference between gain of the absorption tubes and loss of the pyrites = 0.0015 gram.

Having thus ascertained that the products of explosion were carbonic anhydride and water, it was suggested that they might be present in the proportions required by the formula H₂CO₃, and experiments were set on foot to decide the point.

Gravimetric and volumetric methods were employed. The first was essentially the same as that used previously to determine the products of decrepitation, save that various precautions were taken to obtain a greater degree of accuracy, as, for example, drying the pyrites over calcium chloride, after they had been broken into suitably sized pieces, so as to avoid the error that would arise from the presence of water on them (which had come from cavities exposed when the ore had been broken up), bereft of the carbonic anhydride with which it had been previously associated.

The second method consisted in exploding the pyrites in a graduated tube over mercury, and measuring the gas at 100°, and then at the ordinary temperature. The results given by these two methods are compared with those required by the formula H₂CO₃ in the following table:—

	By volume, H ₂ O : CO ₂ .	By weight, H ₂ O : CO ₂ .
H ₂ CO ₃	1 : 1	1 : 2.44
Determined { gravimetrically. 1 : 1.5		1 : 3.75
{ volumetrically.. 1 : 5		1 : 12

These numbers, together with the fact that the first sample of ore (similar to the second in all other respects) contained no water, completely negative the H₂CO₃ theory, and lead to the conclusion that the active factor of the explosion is carbonic anhydride, sometimes accompanied by a variable amount of water, and sometimes alone.

The effect of diminishing the external pressure on the pyrites was then tried, it being thought probable that such a process was likely to cause the decrepitations to take place at a lower temperature, but this proved not to be the case, either when the vacuum was gradually or suddenly produced.

Under the former condition, however, it was noticed that a slight evolution of carbonic anhydride gradually took place without

disintegration of the pieces of ore. A similar result was obtained by passing a current of pure air at ordinary pressure over them, indicating that a process of diffusion went on. By virtue of this, it might be supposed that cavities near the surface would be emptied first, and that as those remaining would have thicker walls, a higher temperature than was normal would be necessary for the decrepitation of the pyrites. Such was actually shown to be the case.

The sp. gr. of the pyrites before and after decrepitation exhibited so little variation, that the pieces could not have contained cavities of any assignable magnitude, and the carbonic anhydride must have been so highly compressed as to exist in the liquid state.

As regards the two specimens of iron pyrites which displayed similar properties, I have proved the presence of carbonic anhydride in one of them, by collecting the gases evolved from it by heating in a vacuum, absorbing the sulphurous anhydride by manganese dioxide, and then the residual gas by barium hydrate. The high temperature at which alone the decrepitations took place, rendered the use of a vacuum necessary, and in the case of the other sample little could be done, as decrepitation did not begin below a temperature sufficiently high to soften combustion glass.

From these various results I conclude:—

(1.) That the decrepitations or explosions are due to the presence of carbonic anhydride (together with water or alone) in cavities in the body of the mineral.

(2.) That the carbonic anhydride is confined at a high pressure, probably sufficient to liquefy it.

(3.) That the water (when present) and carbonic anhydride are not in the proportions required by the formula H_2CO_3 .

(4.) That the carbonic anhydride may be given off either by diffusion through the pores of the walls of the pyrites, or through minute fissures in them, under the influence of a current of air at ordinary pressure, or by the gradual rarefaction of their surrounding atmosphere.

(5.) That the usual temperature at which the pyrites begin to decrepitate is 30° to 35° , but that by emptying the surface cavities of their contents by the diffusion process above mentioned, the necessary temperature is considerably raised, owing to the remaining unemptied cavities being situated farther from the surface, and consequently provided with thicker walls.

(6.) That the explosions that sometimes occur in domestic grates may be due to the coal containing pyrites of a similar character, as pieces of that mineral are commonly found scattered about a room in which such an explosion has occurred.

The analysis gave—

Combined SiO ₂	1·2	per cent.
„ FeO	1·44	„
„ Fe	28·77	„
„ Cu	34·14	„
„ S.....	33·89	„
„ Co	traces	„
Total.....	99·44	

The matrix consisted almost entirely of Al₂O₃ and SiO₂.

LXIV.—*The Specific Action of a Mixture of Sulphuric and Nitric Acids upon Zinc in the Production of Hydroxylamine.**

By EDWARD DIVERS, M.D., and TETSUKICHI SHIMIDZU, M.E., Imperial Japanese College of Engineering, Tokio.

ZINC dissolves in dilute nitric acid, forming nitric oxide, nitrous oxide, ammonium and zinc nitrates, a little nitrogen, and sometimes a trace of hydroxyammonium nitrate. Should it dissolve so far as to neutralise or nearly neutralise the acid, zinc nitrite is also formed. By mixing much sulphuric acid with the nitric acid, the dissolution of the zinc produces sulphates in place of nitrates and nitrites, hydroxyammonium and ammonium sulphates, nitrous oxide and a little nitrogen, little if any nitric oxide, and, lastly, hydrogen. When nitric acid, in moderately small quantity relative to the sulphuric acid present, is added to dilute sulphuric acid freely effervescing on zinc, not only are the above nitrogen products formed, but the intensity of the effervescence becomes so greatly reduced as to suggest an inhibitory action by the nitric acid, until consideration is given to the facts that the temperature rises, and the zinc is corroded even faster than before.

To learn more than these already known facts, showing that a mixture of the acids exerts an action which is not the mere sum of the actions of the acids apart, and to endeavour to determine the cause of this difference in action, we have made a great number of experiments. Many of these will not be described now, because the results

[* NOTE.—In this and succeeding papers, the authors use “hydroxylamine” in place of the well-known word hydroxylamine, without any statement as to why they consider a change in the established nomenclature to be desirable.—THE EDITOR.]

obtained have led to other experiments which supersede them. Nor shall we treat our subject in the order in which we followed it experimentally, but place our observations in what now appears to us the best order to support such conclusions as we have come to. We had hoped to present to the notice of the Society such a valuable memoir on our subject as industry and care seemed likely to enable us to prepare, but in this we have been disappointed, such an undertaking having proved too great for our present resources. We now offer this paper as only a small contribution to the knowledge of the reactions between zinc and the two acids. Of the difficulties we have met with, we shall say more in a later part of the paper.

Rate of Action of Sulphuric Acid upon Zinc.

Experiments made to ascertain the weights of zinc dissolved by the separate acids, as compared with those dissolved by a mixture of the acids, have given important results. Those yielded by zinc and sulphuric acid only have an interest independent of the purpose for which they were instituted.

"Every one knows that, in making hydrogen, more gas is obtained, within certain limits, if the acid be stronger, the temperature higher, the quantity of zinc greater, and the time during which the action continues longer; but what relation the quantity of gas bears to each of these conditions is at present wholly unknown." (A. Vernon Harcourt.) This statement, made nearly 20 years ago, may, so far as we know, be as truly made to-day as when it was uttered. Writing on such a familiar subject as this, we may add, in continuation, that "every one knows" how capricious the reaction of zinc and dilute sulphuric acid appears to be, sometimes setting in almost fiercely, and at others manifesting itself so deliberately as to try the patience of the operator needing the hydrogen. And scarcely less well known is the dictum that the zinc is the more resisting the purer it is, so that with absolute purity we should expect complete passivity. But that the variation in the activity of zinc would be so great as it has proved in our hands, and so sensitive to inappreciable variations in the circumstances under which this activity is developed, will hardly have been inferred by any one.

A large piece of sheet zinc was procured, which had formed part of the lining of a packing-case. It was merely tarnished and spotted by rain on one side, and uniformly, but slightly, weathered on the other. Rejecting a large margin of it all round, the sheet was cut into rectangles 128×86 mm., approximately. For about 45 hours, these pieces were kept wholly immersed in weak alcoholic potash, to cleanse them from grease and oxide. They were then rinsed, pressed between

folds of blotting paper, and gently heated for a minute, in order to dry them thoroughly and quickly. They then presented a uniform and satisfactory appearance, with one side duller than the other, as at first. A small hole was pierced in each, near one margin, that it might afterwards be suspended by a string. Those to be used were weighed, and then fitted with a loop of string. Throughout the preparation of the sheets after they had been immersed in the potash, care was taken not to touch them with bare fingers, except lightly at the edges. The approximate area of the surfaces of a sheet was 22 square decimeters, and mean weight 21.527 grams, with the range of a third of a gram, excepting one sheet which weighed only 20.96.*

The dilute sulphuric acid needed was made in large quantities at a time. The degree of dilution was such that 100 c.c. contained about 15 grams of hydrogen sulphate. Each sheet was wholly immersed in a separate and similar vessel, containing 2400 c.c. of the acid. The quantity of acid was thus so large, relative to the amount of metal dissolving during the experiment, that the diminution of its strength during the progress of the experiment had, and could have, no practical effect in modifying the results. Indeed, in some cases, where a solution was used over again, as a convenience, the strength was still essentially unchanged, for the fresh solution was calculated to be sufficient to dissolve 234 grams of zinc, and had only dissolved when taken for second use a quantity less than 1 gram. Time observations were made with care, and a very few seconds must have been the limit of error. In some cases, the limit was certainly much narrower, because experiments were made simultaneously in this way:—When two sheets were to be immersed, they were held by their loops over their vessels, one in each hand, and then both immersed and the time taken all at once, and by one operator. In a similar way, they were taken out, and plunged into water or fresh acid, according to the plan of the experiment. Or else, two sheets were immersed and removed together, by hanging two on the ends of a glass rod held horizontally in one hand over two vessels of acid; in this way three or four sheets could be tried at once, by using both hands. In rinsing the sheets, the string-loop was quickly removed by scissors. After rinsing, the sheets were pressed again between folds of blotting-paper and dried, as at first, before weighing. Although in most cases a black residue coated the sheets, easily rubbed off, it did not visibly come off on to the blotting paper, and, even had it done so slightly, the accuracy of the experiment would not have been affected, since we only weighed to centigrams. The experiments were made in cold weather. The rise in temperature of

* Sheet-zinc is far from being of uniform thickness throughout the piece.

the mixture during reaction was but slight, in consequence of the large volume of the solution.

One of the sheets of zinc was immersed for five minutes in 2400 c.c. of acid and then weighed. It was again immersed for five minutes in another 2400 c.c. of acid and weighed; and again in a third and in a fourth quantity of acid. The losses in weight were successively—

1.04, 2.08, 3.21, and 5.00 grams,

making a total of $11\frac{1}{2}$ grams in twenty minutes.

A second sheet was treated in the same way, except that a fifth immersion of five minutes was made, and caused it to be eaten away at the edges and into small holes, and therefore to be diminished in extent of surface. The losses were—

0.43, 1.26, 2.39, 4.25, and 7.00 grams,

or in twenty minutes $8\frac{1}{2}$ grams, and in twenty-five $15\frac{1}{2}$.

Four sheets were immersed at once in four vessels of acid, and in five minutes transferred, one to water, the rest to fresh acid, 2400 c.c. in each vessel as before. Again in five minutes the three sheets were removed, one to water, the other two to two of the vessels of the acid already used once in the first five minutes, and still as good as fresh acid. In five minutes more these two were removed, the one into water, the other into one of the vessels of acid already used once in the first five minutes. The losses for sheets A, B, C, and D are given in the table. Four sheets, A', B', C', and D', were similarly treated.

Time.	Sheet.	Loss.	Sheet.	Loss.
5 minutes....	A.	0.55 gram	A'....	0.23 gram.
10 " 	B.	2.08 grams	B'....	1.74 "
15 " 	C.	6.27 "	C'....	2.99 grams.
20 " 	D.	9.65 "	D'....	11.03 "

These experiments with four sheets are free from the objection that might be raised against those conducted on a single sheet, namely, that the surface of the zinc may have been materially affected in some way by the exposure to air during the intermediate drying and weighing, and they thus serve to show that the single sheet was not appreciably affected in the way suggested.

The results of the preceding experiments may be tabulated, so as to make more prominent the wide variation in the quantities dissolved in equal times of equal-sized pieces of the same large sheet of zinc.

5 min.	10 min.	15 min.	20 min.
0·23	1·69	2·99	8·33
0·43	1·74	4·08	9·65
0·55	2·08	6·27	11·03
1·04	3·12	6·33	11·33

The quantity of zinc dissolved in a given time is here seen to have been in one case $1\frac{1}{3}$, or $2\frac{1}{3}$, or 2, or $4\frac{1}{2}$ times what it was in another; taking the extreme results with the ten sheets, whilst in other cases the quantity dissolved in one closely approached that dissolved in another.

It will also be seen how greatly the rate of dissolution increases with the duration of the immersion, and how variable this rate of increase may be in different cases. Thus, while in one case 5 grams were dissolved in the fourth five minutes against 2 grams off the same piece in the second five minutes, in another case $4\frac{1}{2}$ grams were dissolved in the fourth five minutes against $1\frac{1}{4}$ grams in the second five minutes. If a comparison is made of the zinc dissolved in the first five minutes, this difference will be seen to be even much greater.

An acid more dilute than the very strong 15 per cent. acid gave results showing more remarkable disproportion in the quantities of zinc dissolved in equal times under apparently the same conditions. Two sheets cut from a piece of zinc, not the same as that of the previous experiments, lost by 15 minutes' immersion in acid, the one in 15 per cent. acid 6·72 grams, the other in $7\frac{1}{2}$ per cent. acid only 0·57 gram. The experiment repeated with fresh vessels of acid and fresh sheets of the same zinc gave almost identical results—6·72 and 0·56 grams, thus not only confirming those first obtained with this zinc, but contrasting in their uniformity with the varied results obtained with the other zinc, and for no evident reason.

We knew that all zinc could not thus be inactive to acid—that is, could not have more than 20 decimetres of surface exposed for a quarter of an hour to a $7\frac{1}{2}$ per cent. solution of sulphuric acid measuring nearly $2\frac{1}{2}$ litres, and yet only lose half a gram in weight! We therefore repeated the experiment, using other zinc. This time the result was no less surprising, but in a different way. In 15 per cent. acid one sheet lost 4·30 grams, and in $7\frac{1}{2}$ per cent. acid the other lost 2·43 grams, that is actually a little more than half as much as the one in the acid of double strength. A fresh sheet of the zinc that had lost in 15 minutes only 0·56 gram in 7 per cent. acid against 6·72 grams in 15 per cent. acid, was immersed for 20 minutes in 3 per cent. acid, and found to lose only 0·09 gram. A sheet cut from still another piece of zinc lost, when immersed for 15 minutes in 3 per cent. acid, ten times as much, namely, 0·90 gram.

The experiments described were not executed in the order in which we have here given them. Those first given, in which on two occasions a single sheet was immersed repeatedly, and again on two occasions, in which four sheets were immersed at the same moment, were our last ones. The others preceded them, and had led us to the conclusion that the differences in activity we had observed were due to our having used different makes of zinc, so that when we instituted our later experiments with sheets all cut from one piece of zinc and prepared alike and together, we fully expected to get uniform behaviour from these sheets. How far we were from doing so has been pointed out, and, seeing how pieces of the same zinc may differ widely in chemical activity, we must now add that what we had to treat as different makes of zinc because we had found them behave differently and had received them in separate pieces, may after all have been actually or essentially all of one make. Before we had recognised this, we had analysed the active and inactive zinc, and found no key to their difference in the degree and nature of their impurities. The selected specimen of active zinc contained 1.09 per cent. lead, the inactive zinc 1.22 per cent. lead. They both contained a very little iron, something less than 0.1 per cent. The active zinc gave indications of the presence of a trace of arsenic, the inactive hardly gave such indications. We shall have more to say later on respecting the influence and want of influence of the impurities of zinc on its activity.

Granulated zinc also sometimes shows remarkable differences in activity towards sulphuric acid, and this is of special importance in our present inquiry, because we have employed the zinc in this form in nearly all experiments on the reduction of nitric acid by zinc. We have, however, not attempted any quantitative determinations of these differences. All the granulated zinc we have employed in our experiments, and the quantity has been large, has been granulated by ourselves, and we soon found the necessity there was to keep the several batches apart, in order to get uniform results in comparative experiments. We shall return to this question in another section of this paper, and will only mention here that while a granule from one batch would at once set up effervescence when thrown into dilute sulphuric acid, one from another batch would remain passive perhaps for several minutes, and then only very gradually become active.

We do not believe that we have anything new to add in explanation of the great variability in activity of zinc towards sulphuric acid. The current view is probably correct, that pure zinc would prove to be passive in dilute sulphuric acid, and that ordinary zinc becomes active by the formation of innumerable minute galvanic couples on its surface. The temporary passivity, and the irregular rate at which

this is overcome by the acid, as well as the continuously increasing rate at which the acceleration in activity occurs, may be attributed to differences and changes in the degrees of contact of the zinc with the particles of the lead or other foreign metal. By rolling and cutting, or by surface tension brought into action during granulation, the metal becomes compressed on the surface, and intimate contact is made between the heterogeneous particles forming it. Electric polarity can therefore be but slightly preserved between these particles, and so the zinc shows itself nearly inactive for a time. Dissolution of the zinc, however, partly insulates the particles of lead, which then can form couples of marked power with the zinc, and increase the rate of its dissolution. Thus, as dissolution proceeds, more couples are brought into activity, and those already active rendered more so, with the result of causing an ever-increasing rate in the dissolution of the zinc.

With zinc so variable in activity towards sulphuric acid, it does not seem possible to determine with any certainty the relations of the amount of action between the metal and the acid to the extent of their contact, to the dilution of the acid, to the volume of the solution, temperature, time, and other circumstances. There are, moreover, other obstacles to the attainment of trustworthy measurements of the influence of these circumstances. The uniform movement of the liquid over the metal surface, which would be necessary for such purposes, is unavoidably interfered with by the varying extent of effervescence, and by variations in temperature caused by the reaction itself. Uniformity of temperature is also impossible, for although external application of heat or cold may effect something, it can hardly influence the great changes in temperature which must occur at the very surface of contact of the metal and acid, where, of course, the chemical action takes place, and is subject to modification. It seems unnecessary to extend this statement of obstacles.

Rate of Action of Nitric Acid upon Zinc.

Experiments were made with nitric acid similar to those with sulphuric acid, already described. Zinc, size of sheets, preparation of the zinc, volume of the dilute acid, vessels, &c., were the same, but in place of the 15 per cent. solution of sulphuric acid, a solution of 5 grams of hydrogen nitrate in 100 c.c. was used. The results were not remarkable for their differences, as were those with the use of sulphuric acid.

A single sheet was immersed four times for five minutes successively, each time in a different vessel of the nitric acid (2400 c.c.), and

washed, dried, and weighed between each immersion. Another sheet was similarly treated. The losses sustained were—

I.....	2.99	3.69	4.02	3.12
II.....	3.16	3.46	4.02	3.59

making totals, I, 13.82; II, 14.23 grams; or in 15 minutes from the beginning, I, 10.70; II, 10.64. The zinc does therefore vary in activity according as it has been a longer or shorter time in the nitric acid, but much less so than when the acid is sulphuric acid. In the fourth five minutes, the activity proved to be distinctly *less* than it had been, a result due apparently to the mechanical protection given to the unattacked metal by a coat of residual lead, as well as to diminished size of the sheet through its having corroded into holes and at the edges.

The vessels of acid already used* in the first of the two experiments were ranged in a row, and four sheets of zinc immersed, one in each, for five minutes, and the losses weighed.

III, 2.84; IV, 2.55; V, 2.42, and VI, 2.61 grams,

were respectively lost, showing what small deviations from uniformity are found as compared with those when sulphuric acid acts upon zinc. During the reaction there was in every case moderate effervescence and a faint smell of nitrous vapours, but no distinct red fume.

Using a 1 per cent. nitric acid, the loss by the zinc was more variable, but our experiments were not of such accuracy as to justify us in giving their details. The quantity dissolved was often about a fifth of that dissolved in the first five minutes by the 5 per cent. nitric acid, but sometimes less.

Rate of Action of the Mixed Acids upon Zinc.

The rate of action of the mixed acids upon zinc is very different from the sum of the rates of action of the separate acids. This important fact is shown by the experiments which follow.

Two sheets of zinc were first immersed for five minutes, each in its own vessel, in 2400 c.c. of 15 per cent. sulphuric acid, in order to measure, and at the same time to raise, its activity. Sheet I thus lost

* The acid, already once used, was perhaps a twentieth less strong than at first, and certainly slightly weaker in one than in another vessel, but the results show the unimportance of these differences, so great was the excess of acid over that required. It was used instead of fresh acid, merely for convenience and economy, the purest commercial acid having been taken, and that is rather costly here in Japan.

0.43 gram, and sheet II 0.50 gram. They were then immersed for a second five minutes, this time in the mixture of three measures of 15 per cent. sulphuric acid and one measure of 5 per cent. nitric acid, 2400 c.c. to each sheet in a separate vessel.

Of sheet I, 10.11 grams dissolved, and of sheet II, 8.67 grams dissolved in the five minutes. With such a rate of dissolution, we saw that the power of the acid solution might have become markedly less in the course of five minutes through the destruction of much of the nitric acid, and the neutralisation by zinc, ammonia, and hydroxyamine of say 20 grams of sulphuric acid. Influencing the rate of dissolution of the zinc in an opposite way, there was to be considered the effect of the perhaps material, though unnoticed, rise of temperature which might have occurred. We therefore made two other experiments, differing from the preceding only in 8000 c.c. of the mixed solutions being taken instead of 2400 c.c. in each case. The rise in temperature was here, as in earlier experiments, not greater than 2° , and the slight weakening of the solution in the five minutes became now insignificant for our purpose. By the preliminary treatment with 15 per cent. sulphuric acid, sheet III lost 0.51 gram, and sheet IV 0.23 gram. In the mixture, III lost 10.88 grams immersed five minutes in 8000 c.c., and IV lost 11.56 grams by a similar immersion in another 8000 c.c. Further immersion of these sheets in the mixed acids caused their entire dissolution in three or four minutes.

The mixture of acids which thus in five minutes dissolves about 11 grams of zinc from a surface of 2.2 cub. decim. *is of a strength to dissolve not a fifth of this amount if each acid acts independently of the other.* For, as a solution of sulphuric acid, it is only three-fourths of the strength of that which by itself dissolves in the second five minutes about 1.5 gram, whilst as a nitric acid solution it has only one-fourth of that which by itself dissolves in the second five minutes about 3 grams. The combined effect should therefore by calculation be $\frac{3}{4} \times 1\frac{1}{2} + \frac{1}{4} \times 3 = 1\frac{7}{8}$, say 2 grams of zinc dissolved.

Before proceeding to discuss the nature of the great difference between the acids when apart and when mixed, in their power to dissolve zinc, we shall detail some experiments on the duration of effervescence, which agree as to their results with those we have just described.

On the Shortening of the Duration of the Effervescence between Zinc and Sulphuric Acid by adding Nitric Acid.—Not only does the addition of nitric acid to sulphuric acid lessen the degree of the effervescence with zinc, but it materially shortens its duration. This is rendered certain by the experiments on the rate of dissolution of zinc in the mixed acids, but its exhibition by direct experiment is not unimportant.

In each of eight experiments, we poured 250 c.c. of a solution of sulphuric and nitric acids upon 45 grams of granulated zinc, and noted—the time at which we did so, the time when effervescence practically ceased, and the temperature of the mixture, at starting, at six minutes, at ten minutes, and at fifteen minutes. In every experiment, the quantity of sulphuric acid was 10·7 grams. The quantity of nitric acid was very much less, and varied, being 1·375 gram in (I), seven-tenths of this in (II), five-tenths in (III), three-tenths in (IV), one-tenth in (V) and in (VA), and none at all in (VI) and in (VIA). The largest quantity of nitric acid used was to that of the sulphuric acid as one equivalent to ten. In six of the experiments the solution was poured on cold, but in the two marked (Δ) it was poured on warm, and the temperature of the mixture artificially maintained equal to that of experiment (I) as near as might be. We give the results in tabular form:—

No.	Nitr. acid.	Efferv. over.	Temperatures.			
			0 m.	6 m.	10 m.	15 m.
I....	1·0	12 m.	10°	40°	41°	—
II....	0·7	20 „	„	38	40	—
II....	0·5	26 „	„	35	37	—
IV....	0·3	34 „	„	30	32	35°
V....	0·1	44 „	„	26	30	32
VI....	0·0	53 „	„	23	27	29
VA....	0·1	32 „	„	made 40° to 42° throughout.		
VIA....	0·0	35 „	„	made 40° to 42° throughout.		

The effect of the nitric acid in raising the temperature is very marked, and the repetition of (V) and (VI), as (VA) and (VIA), shows the very considerable effect of increased temperature in shortening the duration of effervescence. But when the (Δ) experiments are compared with the first two or three experiments, with which they agreed in temperature, the effect of the nitric acid in shortening the time of effervescence is seen to be still very marked, independently of any change in temperature.

It thus appears that, even after allowance is made for the effect of greater rise in temperature during the action of the acids upon the zinc, the presence of nitric acid greatly hastens the neutralisation of sulphuric acid by zinc.

The Nascent Hydrogen and other Hypotheses in Explanation of the Action of a Mixture of Sulphuric and Nitric Acids upon Zinc.

All the ways that can be suggested as those in which the acids

may prove to be more active towards zinc when mixed than when separate, appear to be included in the following :—

- I. Nitric acid promotes contact of the sulphuric acid with the zinc by consuming its liberated hydrogen while yet nascent.
- II. Sulphuric acid hastens the reduction of the nitric acid by the zinc, by decomposing nitrates, and thus keeping it free.
- III. Sulphuric acid so acts upon the zinc as to make it more active towards the nitric acid.
- IV. Nitric acid so acts upon the zinc as to make it more active towards the sulphuric acid.
- V. Sulphuric acid intensifies the action between the zinc and the nitric acid, by acting upon the nitric acid and combining with it.
- VI. Nitric acid intensifies the action between the zinc and the sulphuric acid, by acting directly upon the sulphuric acid.

We proceed to consider whether, and to what extent, the dissolution of the zinc is quickened in each of these ways, taking them in the above order.

I. *As to Nitric Acid Promoting Contact of the Sulphuric Acid with the Zinc by Consuming its Liberated Hydrogen while yet Nascent.*—The phenomena observed on adding a little nitric acid to sulphuric acid effervescing on zinc, naturally suggests that hydrogen continues to be developed, but is now seized by the nitric acid before it has time to become gaseous. But the difficulties in the way of accepting the nascent hydrogen hypothesis have already been stated in part (this Journal, **43**, 443). In some cases it offers an explanation of the formation of bodies which in other cases are certainly formed without the aid of nascent hydrogen. Ammonia is abundantly produced from nitric acid by the zinc-tin metals in absence of sulphuric or other acid. Hydroxyamine is formed from nitric oxide by a mixture of stannous chloride and hydrochloric acid (v. Dumreicher), and such a mixture never liberates hydrogen. If the action of sulphuric acid upon zinc in the presence of nitric acid subserved the reduction of the latter to the extent required, by supplying nascent hydrogen, no hydrogen gas should escape from a mixture of not more than 7 mols. of sulphuric acid to 2 mols. of nitric acid, when acting upon zinc; yet, as a fact, it escapes freely when the proportion of sulphuric acid is much smaller. This objection to the nascent hydrogen hypothesis, which was insisted upon in the paper already referred to, seems to be of the weightiest character, for at the moment the hydrogen of the sulphuric acid is nascent, it is perfectly mixed with the nitric acid, which it fails to reduce.

There is, however, an explanation, which it is possible to offer, of

this hypothesis. This is, that nascent hydrogen may resemble ozone when exerting its activity, and combine in part only with other bodies and in part become ordinary inactive gas. But then, the invariable univalency of the hydrogen-atom seems of itself sufficient to negative this supposition. Besides, were nitric acid thus able to take merely a certain fraction, such as a third, of the nascent hydrogen, leaving the rest to become gaseous, it should be possible to greatly increase, if not double, the rate of the reduction of the nitric acid, by doubling the quantity of sulphuric acid mixed with it. That this is by no means the case will be shown in a later section.

In contact with zinc, nitric acid, when alone, is rapidly converted into ammonia and other reduction-products. For the nascent hydrogen hypothesis to be true, it seems necessary to assume that in presence of sulphuric acid, nitric acid ceases to be reduced by zinc directly, and suffers reduction instead by the nascent hydrogen of the sulphuric acid. But, as we have already described, the sulphuric acid in contact with zinc is much more rapidly neutralised in presence of nitric acid than in its absence, and the zinc is much more rapidly dissolved. The hypothesis affords no explanation of this rapid action, and the nitric acid evidently does not wait for hydrogen to be liberated by the simple action of the sulphuric acid upon the metal, but either acts freely itself upon the zinc and thereby suffers reduction, or makes, in some way, the action between the zinc and sulphuric acid much more intense, and thus a more prolific source of hydrogen than it is ordinarily.

One way out of the difficulty suggests itself, but this will not stand careful consideration. The hydrogen being consumed in the nascent state by the nitric acid instead of becoming gaseous on the surface of the zinc, the zinc will remain in contact with the solution instead of being kept apart by a layer of gas, and will therefore be dissolved more rapidly. But it will quickly be seen that the thinnest layer of gas would be as effective in breaking contact between the metal and the liquid as the thickest, and in all cases there must be a superabundance of gases developed to operate in this way, if they ever do so. Further, a layer of liquid in contact with the metal must almost at once become inactive, and need removal if activity is to be maintained; so that, pretty certainly, it might be anticipated that the brisker the effervescence the more rapid would be the dissolution of the zinc, in consequence of the more rapid conversion of the liquid, and the consequent change of contact. As a matter of fact, we find that, even when the temperature is equalised as far as possible, one solution of sulphuric acid is neutralised by zinc in rather *less* than the time taken by an equal volume of another solution of sulphuric acid, of only half the strength, acting upon the same extent of

zinc-surface, neutralisation being estimated by cessation of effervescence.

Thus it appears that the nascent hydrogen hypothesis is not only inadmissible, but is quite insufficient to explain the special activity of the mixed acids.

II. *As to Sulphuric Acid Hastening the Reduction of the Nitric Acid by the Zinc, by Decomposing Nitrates and thus keeping it Free.*—When nitric acid alone acts upon zinc, by far the greater part of it is converted to zinc nitrate, and a little to ammonium nitrate. By decomposing these salts, and thus leaving the unreduced nitric acid free, sulphuric acid will undoubtedly hasten, to a certain extent, the reduction of the nitric acid, and, since nitric acid is more active towards zinc than its equivalent of sulphuric acid, will also hasten the dissolution of the zinc. But the experiments described show clearly the insufficiency of this action of the sulphuric acid; for in them nitric acid has been present in such abundance as to render the small quantity of it fixed as nitrate of no practical account. And, besides, the mixture which has proved so active contained in a given volume only a fourth of the nitric acid present in the much less active solution of this acid by itself.

The hypothesis advanced by Deville, and maintained by one of us in a previous paper, that the acids, when mixed, act upon zinc just as if they were not mixed, cannot, therefore, be accepted as sufficient to explain the special power of the mixture, although it is partly true. The evolution of hydrogen by the mixture shows that the sulphuric acid exerts at least to some extent its proper action upon the zinc. The formation of ammonia, from the first moment of the reaction, shows that the nitric acid also exerts its proper action, as we shall endeavour to establish in a later section, and by further evidence which we hope to give in a forthcoming paper.

III. *As to Sulphuric Acid Acting upon the Zinc so as to make it more Active towards the Nitric Acid.*—As the action of an acid upon zinc proceeds, it becomes accelerated by the increasing galvanic differentiation of the surface of the metal; but the effect of nitric acid in increasing the activity of the zinc towards fresh portions of the acid, appears to be much greater than that of sulphuric acid, and we, therefore, think that the effect of sulphuric acid in this way is quite unimportant.

IV. *As to Nitric Acid Acting upon the Zinc so as to make it more Active towards the Sulphuric Acid.*—In order to test the relative power of nitric acid in developing in zinc activity towards sulphuric acid, we have immersed for five minutes sheets of zinc, cut and cleaned as for our other experiments, in 2400 c.c. each of 5 per cent. nitric acid, and have then submitted them to the action of 15 per cent. sulphuric

acid. Of two sheets immersed, one in 5 per cent. nitric acid and one in 15 per cent. sulphuric acid, the former lost in five minutes 2.68 grams, the latter 0.15 gram; then immersed for a second five minutes, both in 15 per cent. sulphuric acid in separate vessels; the former lost 1.12 grams and the latter 0.99 gram. The experiment was repeated with fresh materials. A sheet five minutes in 5 per cent. nitric acid lost 2.71 grams, and another in 15 per cent. sulphuric acid lost 0.23 gram. Again immersed, this time both in 15 per cent. sulphuric acid, the former lost 1.38 gram, and the latter 1.00 gram.

The advantage thus lay with the nitric acid preparation, but not to any great extent, and this advantage seems to be more than accounted for by the much greater extent to which the zinc had been corroded by the nitric acid than by the sulphuric acid.

As in the mixed acids the concentration of the nitric acid was only a fourth of what it was in these experiments, its greater corroding effect should have been unimportant when thus reduced. This explanation of the wonderfully high activity of the mixture seems therefore to be insufficient.

V. *As to Sulphuric Acid Intensifying the Action between the Zinc and the Nitric Acid, by Acting upon the Nitric Acid and Combining with it.*—By regarding nitric acid as ammonia, with oxygen and hydroxyl replacing its hydrogen, we may conceive of sulphuric acid forming a salt with it, as it does with nitrosyl. But as there is no evident reason why such a salt should be more active towards zinc than free nitric acid, it is useless to speculate further in this direction.

VI. *As to Nitric Acid Intensifying the Action between the Zinc and the Sulphuric Acid by Acting Directly upon the Sulphuric Acid.*—This hypothesis we discuss and uphold in the next section.

Nitric Acid and Zinc Exert a Specific Combined Action upon Sulphuric Acid.

There seems to us but one explanation which fully accounts for the specially great activity upon zinc of a mixture of nitric and sulphuric acids, and that is, that the sulphuric acid, perhaps inactive to zinc alone (if pure), and certainly inactive towards nitric acid alone, is freely decomposed by contact with the two at once, its hydrogen going to the nitric acid, and its sulphate radical going to the zinc. Just as neither stannous chloride nor nitric oxide can alone decompose hydrochloric acid, while together they do so without difficulty, so together nitric acid and zinc act freely upon sulphuric acid, although apart they may have little or no action upon it. There will always, indeed, be some little action between the zinc and sulphuric acid only, and much probably between the nitric acid and the zinc, but these actions are independent.

of and accidental to the specific action of the zinc and nitric acids upon the sulphuric acid, with which they are concurrent.

There must, of course, be a like specific action of tin and nitric acid upon sulphuric acid or upon hydrochloric acid, and in this case, whereas the combined action is very great, the separate actions, particularly that of the sulphuric or hydrochloric acid upon the tin, are very slight. Again, there is the specific action, pointed out in another paper (this Journal, 45, 194), of a mixture of selenium and cold sulphuric acid upon hydrochloric acid, in which the chlorine of this acid goes to the selenium and the hydrogen to the sulphuric acid, which it reduces.

That the theory here advanced is quite adequate to explain the rapid action of the mixed acids upon zinc, is evident. That it may well account for the production in the mixture of hydroxyamine, only found in traces when nitric acid alone acts on zinc, must be equally admitted. The trace of hydroxyamine found when only nitric acid is used, may well be due to the presence of traces of other acids, and then the specific action of the mixture becomes sharply differentiated by its products from the separate action of the zinc upon the nitric acid.*

It need hardly be added that this theory applies to all changes commonly treated as the effects of nascent hydrogen, and that, in all of them, therefore, it is held that the reductions effected are unconnected with the production of free hydrogen. Hitherto the power of the zinc-tin class of metals to act like stannous and ferrous salts as hydrogenising agents, although with greater intensity, has been passed over unnoticed, because of the additional power they possess of actually liberating hydrogen. But the facts, as now ascertained by us, require that the two modes of action by these metals should be admitted as distinct.

Nascent hydrogen is an imaginary reagent only.

Without pretending to be able to give any precise explanation of the peculiarity and different power of different hydrogenising mixtures, of which a metal is a part, we consider that the theory here propounded makes these peculiarities and different powers more intelligible than they are on the nascent hydrogen hypothesis. Thus, that nitrobenzene gives the *base*, aniline, to an *acid* reducing mixture, and not to a basic mixture such as sodium and water; that the *base*, hydroxyamine, is formed in *acid* mixtures, and the *acid*, hyponitrous acid, in *basic* mixtures, seem natural events when we regard the substances in the mixture as exerting their characteristic influence, whereas, considered as the varying effects of the contact of nascent

* For additional remarks on this point, refer to the next section but one after this.

hydrogen, they seem inexplicable, unless we assume that such nascent hydrogen bears upon itself in each case the marks of its origin.

There is one point in the view here taken of the nature of the reduction of nitric acid by sulphuric acid and zinc, which needs consideration, and that is the liberation of free hydrogen which takes place, even when the sulphuric acid is not in undue quantity. Could nitric acid be completely changed into hydroxyamine by this reaction, just seven equivalents of sulphuric acid would be required, six being for the zinc and one for the hydroxyamine. But with such a proportion of the sulphuric acid hydrogen is freely liberated. The explanation appears clearly to be this: much, even half, of the nitric acid in contact with the zinc at any moment attacks the zinc direct, leaving for the instant a corresponding part of the sulphuric acid touching zinc in absence of nitric acid; this part of the sulphuric acid partly attacks the zinc and yields free hydrogen, and partly, principally no doubt, attacks the zinc nitrate, reproducing nitric acid. Thus, the separate action of the nitric acid upon the zinc brings about a certain degree of the action of the sulphuric acid alone upon the zinc.

Hydroxyamine in Acid Solution is not Reducible by Zinc.

In the paper "On the Production of Hydroxylamine from Nitric Acid," tabulated results are given, from which it can be seen that, on leaving a mixture of nitric acid and either sulphuric or hydrochloric acid upon zinc, hydroxyamine is both produced and destroyed. In the course of many experiments since made, we have further observed, in the first place, that a sufficient excess of sulphuric acid being used, that is, ten equivalents or more to one of nitric acid, the maximum amount of hydroxyamine, when reached, remains unchanged for several minutes longer, and, in the second place, that its amount only begins to diminish when the sulphuric acid has become much neutralised. We give a few examples of our testings in illustration of this.

Zinc 36 grams, nitric acid 1 gram, sulphuric acid 60 equivalents (to 1 nitric acid) or 47 grams, dilution to 400 c.c., temperature $11\frac{1}{2}$ —53°; at 9, 13, and 17 minutes there was always the same quantity of hydroxyamine found present, equivalent to 0.45 gram nitric acid.

Zinc 18 grams, nitric acid 1 gram, sulphuric acid 15 equivalents, dilution to 200 c.c., temperature 9—34°; at 13, 15, and 17 minutes there was the same quantity of hydroxyamine found, also equivalent to 0.45 gram nitric acid.

Zinc 36 grams, nitric acid 1 gram, sulphuric acid 15 equivalents, dilution to 400 c.c., temperature 9—25°; at 16, 18, 20, and 22 minutes

there was found the same quantity of hydroxyamine, equivalent to 0.42 gram nitric acid.

These are some of the experiments performed with one kind of zinc, rather weak as a means of producing hydroxyamine (see the next section but one to this). With more productive zinc the steadiness of the quantity of hydroxyamine is less prolonged.

It is hardly necessary to give fresh examples of the other point observed, namely, the descent in the quantity of hydroxyamine as the time when effervescence ceases is approached and passed, because many were given in the other paper. We give here therefore, just one out of many more.

Zinc 36 grams, nitric acid 1 gram, sulphuric acid 10 equivalents, dilution to 200 c.c., effervescence ceasing at 13 minutes; the hydroxyamine found at 10, 13, $17\frac{1}{2}$, and 32 minutes was successively equivalent to 0.48, 0.44, 0.36, and 0.26 gram nitric acid.

An explanation of the steadiness of the quantity of hydroxyamine for some minutes, readily *presented* itself, being that hydroxyamine was undergoing destruction at the same rate as nitric acid was being converted into it. But we found that, although traces of nitric acid lingered on afterwards, almost all of it had disappeared by the time that the hydroxyamine reached its maximum amount, and this seemed to show that hydroxyamine was stable for a time in the solution. Decisive testing was not, however, easy, where it was a question of the presence of a very small fraction of a gram of nitric acid (that of a trace being certain) in several hundred cubic centimetres of solution.

The matter was easily settled in another way. To dilute sulphuric acid standing over granulated zinc, a solution of hydroxyammonium chloride of known strength was added and then, after a time, the zinc sulphate solution was titrated for hydroxyamine. In this way it was first found that hydroxyamine could exist for a time with sulphuric acid and zinc without change, and then that by keeping up active effervescence through the occasional addition of acid, hydroxyamine could be left for any reasonable time in such a solution without material change.

In one experiment, of a solution of hydroxyammonium chloride 10 c.c., containing 0.033 gram of hydroxyamine, were made up to 100 c.c. with water, containing a little sulphuric acid. The mixture was poured upon 45 grams of granulated zinc, and thus exposed to a relatively very large surface of zinc. It was left in contact with the zinc for two hours, dilute sulphuric acid being occasionally added, so as to keep up effervescence. The solution, still effervescing, was poured off, and titrated for hydroxyamine, and the whole of this was found unchanged. Indeed, the anomaly was observed, of a little more iodine being required than equalled the whole hydroxyamine. But we

find that, in presence of a concentrated solution of zinc salt, a clear excess of iodine solution is decolorised over that calculated for the hydroxyamine.

We then tried the action of zinc alone upon a dilute solution of hydroxyammonium chloride. Here there was a marked destruction of the hydroxyamine in two hours, one-eighth to one-fourth disappearing. The nitrate appeared to be somewhat more unstable. Acidified with a little sulphuric acid, however, the nitrate gave in ten minutes on zinc, a third *more* hydroxyamine than it contained in consequence of the conversion of part of its nitric acid to that base. (The nitrate consists by weight of one part base to two parts acid, so that about a third of its acid became hydroxyamine.) The presence of zinc sulphate or ammonium chloride or of free ammonia, appears to be without marked effect.

Hydroxyamine is thus seen to be only very slowly decomposed by the contact of zinc with its cold solution, even in absence of acid. It was otherwise, however, in the case of hot solutions, for in these the hydroxyamine is destroyed by zinc with relative rapidity, although still wonderfully resistant to decomposition. Boiled for a quarter of an hour in 100 c.c., and less, of solution, upon 35 grams of zinc, 0.033 gram was reduced to 0.02 gram. Heated to 70–80° for one hour upon 35 grams of zinc, 0.033 gram hydroxyamine in 100 c.c. was reduced to 0.008 gram.

The observed rise, the continuance for a time at a level, and then the decline of the quantity of hydroxyamine, during the reduction of nitric acid by zinc and another acid, are due, therefore, to the nitric acid being partly converted to hydroxyamine during the rise, to the hydroxyamine being stable in an acid solution in contact with zinc, and to its being gradually destroyed when in hot solution by contact with zinc, if no free acid is present. The beginning of its destruction before all the acid is neutralised may be safely attributed to neutralisation having existence close to the zinc, while the body of the solution is still acid. Another point to be explained is that the destruction of the hydroxyamine, in these experiments upon the reduction of nitric acid, is somewhat greater than might be expected from the results obtained with previously prepared hydroxyammonium chloride. There is no difficulty, we consider, in believing this to be due to the "active" condition of the zinc, induced by the previous extensive action of the acids upon it, which leaves it blackened and much corroded. In the direct experiment upon hydroxyamine in absence of acid, the zinc is but little affected, and preserves much of its initial activity.

Ammonia and Hydroxyamine appear to be not Consecutive Products, but Products of Parallel and Independent Reductions.

As pointed out in the previous paper, ammonia is abundant from the first, during the reduction of nitric acid by sulphuric acid and zinc. Its non-production from hydroxyamine, in the presence, that is, of free acid, gives its appearance during this reduction a new interest. Nitrous oxide is also produced. We have made no attempt to estimate the very small quantities of this gas formed in our experiments. Deville's determinations may be referred to on this point, but we ourselves in Japan have no means of doing so, for purposes of illustration.

A few determinations only of ammonia have been made by us, and further work in this direction is desirable. Having poured off the acid solution from the zinc at those times when it was calculated that the hydroxyamine would have just reached its maximum, one part was titrated for hydroxyamine, and another titrated for ammonia, by adding first sodium carbonate until some zinc carbonate was precipitated, then iodine to destroy hydroxyamine, then precipitating nearly all the zinc by sodium sulphide, and distilling the mother-liquor with potassium hydroxide. The ammonia was received in acid and titrated. In this way we obtained ammonia equivalent to much of the nitric acid not convertible into hydroxyamine.

By using a very great excess of sulphuric acid nearly, if not all, the nitric acid unconverted to hydroxyamine appears to be converted into ammonia. This is in accordance with Kinnear's (*Chem. News*, 46, 63) results, and we believe it be correct, but there is difficulty in determining closely a very small quantity of ammonia in presence of very much zinc salt, and, without more trials than we have made, we cannot assert that it is so.

Under favourable conditions, we have got as much as, and even more than, seven-tenths of the nitric acid converted to hydroxyamine, but, with unsuitable zinc, we have sometimes failed to get more than two-tenths converted. In our former paper, we mentioned a yield of eight-tenths of the nitric acid as hydroxyamine, but we were not confident as to this yield having been really obtained.

In a preceding section, we have attributed the production of hydroxyamine entirely to the specific action of the zinc and the nitric acid upon sulphuric acid. We can now almost assert that ammonia is not a product of that specific action, and that the ammonia, freely produced from the first during the dissolution of the zinc in the mixed acids, is formed solely by the direct action of the nitric acid upon the zinc. Uncertainty thus seems cleared away as to the specific hydrogenising action of the sulphuric acid upon the nitric acid. For,

although nitric acid in contact with zinc and water can readily hydrogenise itself without the aid of any other acid, the product is then ammonia, not hydroxyamine, whereas when nitric acid is hydrogenised by sulphuric acid, the product is hydroxyamine and not ammonia.*

In the paper on the production of hydroxyamine from nitric acid, we have said that a perfect metal for making hydroxyamine would be one active towards dilute nitric acid, inactive towards sulphuric or hydrochloric acid, and inactive towards hydroxyamine. With our present knowledge we would alter this, and say, that such a metal should be inactive to nitric acid alone, and active only to a mixture of nitric acid with either hydrochloric or sulphuric acid. The above considerations at once explain why it is that a metal may freely produce ammonia from nitric acid and yet produce hydroxyamine from it only with difficulty, or not at all. For, in such cases, there may be strong action of the metal upon nitric acid, or independently upon both acids, whereby ammonia will be formed, and yet be no specific action upon the two acids combined, which would give rise to hydroxyamine. Or again, the effect of this specific action may be as nothing compared with that of the superior activity of the metal towards the independent acids.

Dependence of the Yield of Hydroxyamine upon undetermined Peculiarities in the Nature of the Zinc Used.

Granulated zinc may differ widely in its power of yielding hydroxyamine, but a given preparation of it, or mixtures of similar preparations, will show under the same circumstances the same power at one time that it has shown at another. The differences observed in this relation between different preparations of granulated zinc, depend in part upon the nature of the zinc melted down, of course, but they also depend upon differences in the process of granulating. Partly, no doubt, in consequence of the fact that apparently both the condition of the zinc before it has been granulated, and the character of the operation of granulating it, may exert marked influence upon its power to produce hydroxyamine from nitric acid, but at any rate

* In our first paper we have said—in support of the view that the reduction of hydroxyamine to ammonia by zinc is due to the metal uniting with the hydroxyamine to form zinc ammonium hydroxide—that such a compound as zinc ammonium hydroxide actually occurs in the hot alkaline solution resulting from the action of hydrochloric and nitric acids upon zinc, and slowly decomposes into ammonia and zinc hydroxide. We would now point out that this soluble alkaline compound may be hydroxychloride of zinc, $\text{HO} \cdot \text{Zn} \cdot \text{Cl}$, produced by the action of hot solution of zinc chloride upon zinc, and therefore the union of zinc with hydroxyamine is as yet hypothetical.

we have failed in the attempts we have made to secure at will granulated zinc of a uniform and high power in this respect, or to ascertain any sufficient knowledge of the causes of its varying power.

On one occasion, there seemed to us to be a marked difference between the same zinc when granulated at different temperatures. By running the zinc when almost boiling hot, and then again, from the same melting, after the zinc had cooled almost to the solidifying point, a much more productive lot of granules was obtained from the second running than from the first. But on trying the effect of this difference in operating again and again, we got no confirmation of our first result. We also varied the process by pouring from a height, and pouring near the water, and of granulating in boiling water and granulating in cold water, but from all our trials we learnt nothing. At one spell of work we could repeatedly granulate zinc turning out to be of nearly equal power, but on another occasion we could not count on producing more zinc of the same power.

Effect of Iron in the Zinc.—It is no doubt impossible to melt zinc in an iron vessel without getting iron dissolved in it, but, with precautions, the quantity may be made so small as to be insignificant if not inappreciable.*

Iron in zinc appears to act injuriously, judging from our experiments. Zinc which had taken up iron by being melted in a wrought-iron pot at a high temperature, had its power to produce hydroxyamine reduced by half. But even zinc from the same stock, but of different granulations, sometimes showed considerable differences without any corresponding differences in iron-content.

Some granulated zinc, which would not give us a greater proportion of nitric acid converted to hydroxyamine than three-tenths, was found to contain as much as 0.67 per cent. of iron, but then a zinc-iron alloy from a galvanising tank, and containing *several units per cent.* of iron,† gave more than two-tenths of the nitric acid as hydroxyamine, and,

* *Note on Granulating Zinc.*—If, as is commonly the case in a chemical laboratory, the zinc is melted in an open wrought-iron ladle coated with black or red oxide, and the temperature allowed to run high, much iron may enter the zinc, which is not surprising. It is nearly certain, for one thing, that iron oxide is readily reduced by melted zinc and dissolved more readily than is the massive iron of the pot. Further, it is well known in galvanising, that wrought iron becomes rapidly dissolved by liquid zinc, and that, therefore, cast iron must be used for the vessels. Zinc rapidly takes up iron from a clay crucible, when heated in it. But we have found that, when a cast iron deep pot is used, scoured clean inside and well black-leaded, and that the pot is kept covered, and is heated on a smart fire until the zinc is only just melted, the zinc can be poured from the pot leaving this clean and with the coating of black-lead almost intact, and carrying with it no iron beyond that already contained in it.

† Analysed by us, but record mislaid.

still more remarkably, a zinc containing only about 0.1 per cent. of iron has given us as low a maximum yield of hydroxyamine as that which contained 0.67 per cent. iron.*

Lead—We melted lead with the zinc in varying small proportions before granulating, and obtained quantities of hydroxyamine with these plumbiferous zincs, which showed no relation to the quantities of lead. One batch of metal containing $2\frac{1}{2}$ per cent. of lead actually gave us some of our best yields (six-tenths of the nitric acid converted to hydroxyamine), but other preparations with about this proportion of lead quite failed to give particularly high yields. Zinc saturated with lead gave low yields, but this fact was due perhaps to the effect of the presence of the lead in lessening the surface of the zinc exposed. We arrived at the conclusion that a little lead had no appreciable influence.

Freshly amalgamated zinc is insensible to the specific action of the mixed acids, so that the action of dilute nitric acid in dissolving such zinc, which is much less than upon zinc without mercury, is not sensibly increased by the presence of sulphuric acid, and hydroxyamine is not formed. At least this is the case for some time, but gradually, under the action of nitric acid, the amalgamation ceases to protect the zinc against the sulphuric acid, and then it dissolves faster, and hydroxyamine is formed. The fact here described is further evidence of the insufficiency of the view that sulphuric acid modifies the action of nitric acid merely by decomposing its zinc salt as fast as it is formed.

When treating of the action of sulphuric acid upon zinc, we indicated the difficulties of carrying out experiments in such a way as to place the influence of each circumstance upon that action clearly and unmistakably in view. The difficulties become much greater when the investigation refers to the action of the mixed acids. The one among them which is possibly insurmountable in any case, and which is certainly so in the circumstances in which we find ourselves, is the fiftful behaviour of ordinary zinc towards the mixed acids, if we may be allowed so to put what, plainly stated, is only our own inability to detect the causes of the diverse behaviour of different samples of zinc. We have not succeeded even in tracing any evident connection between the relative activity of zinc in sulphuric acid and its relative power of generating hydroxyamine from the mixed acids. For before the problem of doing so presented itself to us, we had used up what zinc we had that produced high yields of hydroxyamine,

* Did the iron of ferruginous zinc dissolve in the acid, its destructive activity upon hydroxyamine would be certain, but it is well known that, while zinc is abundantly present, iron does not dissolve in sulphuric acid, and in our experiments, although a little nitric acid was present, no iron was found in the solution.

and could not renew our stock. We can certainly say that a zinc may be very active in sulphuric acid, and yet prove a poor means of getting hydroxyamine. On the other hand, the zincs which gave us very high yields were such as very quickly dissolved in the mixed acids, but whether such zincs would also have been very active upon sulphuric acid alone we cannot say with certainty; all that we can say is that we think it probable they would.

We have, in consequence of this and other difficulties, been unable to carry out, even in part, an investigation which would serve to establish the exact relations existing between the action of sulphuric and nitric acids, and temperature, dilution, varying proportions of the acids, time, and other circumstances. But in our attempt at such an investigation, made for the most part before we had learned how much zinc may vary in its power, we had made observations concerning these relations which seem to be worth recording, although they are insufficient of themselves to establish anything with certainty. Without, therefore, describing in detail what we have done, and tabulating the results of our numerous experiments, we shall summarise such conclusions as we have arrived at.

The apparent Influence of Temperature, Time, Dilution, and other Conditions upon the Reaction between Zinc and Acids.

In hot solutions, hot even to boiling, not only does the action of acids upon the zinc proceed very much more quickly, but *the yield of hydroxyamine is increased*. In accordance, however, with what has already been said about the destruction by zinc of hydroxyamine in hot solution, it should be remembered that the solution must be preserved highly acid while in contact with the zinc. It is consequently not desirable to cool the mixture during reaction, as was indicated in our former paper, but only to guard against the rapid neutralisation of the acids which takes place when they have grown hot. The cause of the beneficial action of heat is probably an alteration in the relative energy of the acids upon zinc, in which case something further may yet be learned through this concerning the specific action of the mixed acids.

The time taken to neutralise a given quantity of an acid, or to complete some other chemical action upon it, such as the formation of hydroxyamine from nitric acid mixed with sulphuric acid, is directly as the dilution of the acid, and inversely as the area of contact between the metal and the solution, other circumstances being equal. It is independent of the quantity of the acid.

It will not be doubted that if in a given volume of a certain dilute acid twice the surface of zinc is exposed in one case that is exposed

in another, the rate of neutralisation with twice the zinc will be twice as great. In practice, however, there are modifying circumstances. Thus, the heating is greater with the larger surface of zinc, and therefore that does its work somewhat more than twice as fast as the smaller surface. Again, twice the weight of granulated zinc of one quality may be considered to expose twice the surface, but in practice it does not always act twice as fast. The reason is this: there are to be considered, in making the comparison, the free surface of the heaps and the cavities of the granules, and the surface of the interstices of the heaps and the cavities of the granules, for the surface of the heaps more rapidly changes contact with the liquid than do the interior surfaces. Now, since the upper surfaces of the heaps in the flasks will be more nearly equal to each other than in the ratio of 2 : 1, it follows that twice the weight of granulated zinc will not be twice as active, except perhaps with violent shaking or violent effervescence. With dilute solutions, twice the weight of granulated zinc was found not able to produce hydroxyamine twice as fast; but with more concentrated solutions it appears to be so, probably because of more violent effervescence, and of shortening of the time required, since differences in rate of action would then be less measureable.

But another remarkable circumstance was observed by us. Using twice as much zinc we generally got a somewhat worse yield of hydroxyamine. If we consider that in the deeper recesses of the heap a little local neutralisation of the acid, with consequent destruction of hydroxyamine, occurred, we have a reason why the deeper heap of granules should unfavourably compare with the other, else it is difficult to conceive how there could have been any difference, and that observed must be referred to errors of experiment. But in several pairs of experiments we got this difference, which was that between 44 and 42, in another case that between 47 and 45, and in a third case, with less dilution of acid, 45 and 44. At any rate, one explanation serves, when the quantity of granulated zinc is doubled, both for the lower yield of hydroxyamine and for the rate of action being slower than that calculated. When the acid is sulphuric acid, its action is certainly not proportionate to its degree of dilution; this we have fully shown in an earlier section.

This fact, however, is sufficiently accounted for by the changing condition of the zinc, galvanic or otherwise, during the action of the acid. With the mixed acids, as well as with nitric acid alone, the proportionate action proves to be so far true on trial as to justify us in believing that it would be strictly so under parallel circumstances. Thus, given a certain quantity of granulated zinc, it was always approximately true in our experiments that double the volume of dilute acids took double the time to reach its maximum content of hydroxy-

amine, or double the time to cease to effervesce, provided shaking the vessels was kept up with practical uniformity.

We have also stated that the time taken to effect a given change is independent of the quantity of the acid, that is, independent of its concentration, within the limits of the occurrence of a common reaction. This proposition seems worthy of separate consideration, although it is but a corollary to that as to the time being proportionate to the volume. It is only experimentally true, or approximately true, when the acid is either nitric acid or the mixed acids. When we poured upon a certain quantity of zinc a certain volume of dilute mixed acids of double the concentration of other mixed acids, both the highest yield of hydroxyamine to be got and the termination of the effervescence were reached in nearly the same time in one solution as they severally were in the other. There was, however, generally a little difference in favour of the stronger solution, in consequence no doubt of the greater rise in temperature.

It is easy to see that, although the completion of a given reaction, such as the neutralisation of the acids or the reduction of all the nitric acid, will take a time dependent only on the dilution and the surface of the zinc, yet the reaction will not proceed to its completion at the same rate. We have scarcely any experimental evidence on this point, but then we have not specially worked for it. The argument is this. Taking as the simplest case that of equal concentration but different volume, it must be that the greater volume will proceed for a time faster to saturation or reduction than the other. For, starting at the same rate of action, because of equal concentration, the greater volume must necessarily diminish in concentration, by equal rate of action, less rapidly than the smaller volume, and soon, therefore, as being the stronger solution, act on the zinc more powerfully than the other. During the latter part of the action, this state of things must be reversed.

There is a consideration in connection with the rates of action of dilute acids upon zinc which bears upon the theory of the specific action of mixed nitric and sulphuric acids. Suppose that zinc were not partly passive towards sulphuric acid, or at least less active towards it than towards nitric acid, then, no matter in what proportion we mixed the acids in a solution, the two ought to get entirely neutralised or decomposed together. But, the sulphuric acid being in sufficient quantity, this does not prove to be the case, more or less of this acid remaining after all nitric acid has disappeared. And yet the mixed acids possess an activity that rivals that of nitric acid itself. Plainly, then, the part played by the nitric acid is not mainly that of acting on the zinc, so as to render it more sensitive to the sulphuric acid than it was, and that part of the sulphuric acid which does not

act specifically with the nitric acid has still to get neutralised in its own slow way.

Another point for consideration is the divided activity of the nitric acid, this acid acting in part directly upon the zinc to form ammonia, even in presence of excess of sulphuric acid, and in part in conjunction with the sulphuric acid to form hydroxyamine. It would seem to follow from this that nitric acid by itself has an activity towards zinc superior to that of the mixed acids, and in consequence acts to some extent directly upon the zinc.

Time of Maximum Yield of Hydroxyamine.—The want of a knowledge when to look for the moment of highest production of hydroxyamine, was a considerable hindrance to satisfactory working. In a further series of experiments we should not feel this difficulty, because we now know that by keeping up free effervescence by adding some more sulphuric acid we need not fear destruction of hydroxyamine to a material extent.

The main circumstances determining the time necessary for reduction of all nitric acid, are the dilution of the nitric acid, the surface of the zinc, and the temperature. Besides may be mentioned the degree of agitation of the liquid through shaking the containing vessel and through the effervescence caused by the sulphuric acid. A greater excess of sulphuric acid somewhat quickens the reduction of the nitric acid, but a sufficient reason for this appears to exist in the more violent effervescence and consequent motion of the liquid, and in the greater rise in temperature.

The Yield of Hydroxyamine is not affected by the Quantity of Sulphuric Acid in excess, but is affected by its Degree of Dilution.—In our former paper on the production of hydroxyamine from nitric acid, we have shown that as the proportion of sulphuric acid is increased from 3 equivalents to 11, so is the proportion of nitric acid converted to hydroxyamine increased. We have since tried the effects of larger proportions still of sulphuric acid. When there is about 1 gram of nitric acid in 200 c.c. of solution, an increase above 14 or 15 equivalents of sulphuric acid appears to have little effect; but when the nitric acid is twice as dilute as this it proves advantageous to increase the sulphuric acid to 20—25 equivalents. Or, to put the matter in another form, the sulphuric acid should be in quantity not less than 5—6 grams in every 100 c.c., and need not be more, unless the quantity of nitric acid should exceed 0.7 gram in the 100 c.c. These proportions are somewhat affected by the quality and quantity of the zinc employed, zinc capable of giving high yields of hydroxyamine appearing to require a somewhat less concentrated sulphuric acid than zinc giving low yields.

Beyond, then, a moderate limit, such as the above, an increase of

sulphuric acid has no effect on the yield of hydroxyamine. Were there only the specific action of the two acids together upon the zinc taking place, just seven equivalents of sulphuric acid would be required. The direct action of the nitric acid upon the zinc would but little affect the quantity of sulphuric acid needed, since the indirect exhaustion of the sulphuric acid through the nitric acid becoming ammonia and nitrous oxide is almost the same as its direct exhaustion in converting the nitric acid to hydroxyamine. But, as we have already said, the direct action of the nitric acid upon the zinc leaves some of the sulphuric acid free to divide itself between zinc nitrate and metallic zinc, with the latter of which it exhausts itself without any effect, direct or indirect, in hydrogenising nitric acid, but evolves hydrogen instead. Now to what an extent the proportion of seven equivalents of sulphuric acid should on this account be exceeded, or even whether it need be exceeded at all, will depend upon the nature of the zinc. For another purpose, however, an excess of sulphuric acid is desirable, and that is to keep the solution a little acid to the end of the reaction with the nitric acid, and still a little longer, in order to guard against destruction of hydroxyamine by zinc.

LXV.—*On the Behaviour of Stannous Chloride towards Nitric Oxide, and towards Nitric Acid.*

By EDWARD DIVERS and TANEMASA HAGA.

THE following account of an investigation we are carrying on, into the constitution of nitric acid and some of the products of its reduction, may serve to illustrate further the statement concerning some of the processes of reduction enunciated in a paper just presented to the Society by Mr. Shimidzu and one of us. That statement is, that a mixture of nitric acid with hydrochloric or sulphuric acid exerts a specific action upon certain metals, an action which is not a mere combination of the separate actions of the two acids. It may also, we hope, when it has been continued in a second communication on the subject, which we are preparing to lay before the Society, serve to throw light on the constitution of oxy-nitrogen compounds.

Reaction between Nitric Oxide and Stannous Chloride.

Every chemist is supposed to know that when nitric oxide is passed into a hydrochloric acid solution engaged in dissolving tin,

ammonia and hydroxyamine are produced. Strictly speaking, however this is by no means the case. We assert that, in the change that goes on, *not a trace of ammonia is formed*. Experience to the contrary must have been all vitiated by neglecting to exclude air while the gas was in contact with the mixture, and to use pure nitric oxide. Hydroxyamine is formed, but if the nitric oxide never comes in contact with oxygen, not a trace, as we have said, of ammonia is formed. V. Dumreicher has already shown (Abstr., 1882, 361) that acid stannous chloride will of itself convert nitric oxide to hydroxyamine; whether he then found ammonia or not we cannot learn. This will have depended upon the care with which he excluded air. But his observation was of great interest at the time, as serving to show what little foundation there was for the hypothesis of the action of nascent hydrogen in explaining the formation of hydroxyamine from nitric oxide by treating it with tin and hydrochloric acid. So far, indeed, as we can ascertain by experiments which we have made, the presence of the metal does not directly help to form hydroxyamine, and is of no service but to generate stannous chloride. It is objectionable on two grounds: it leaves the solution charged with unused stannous chloride whenever the preparation of hydroxyamine is stopped; and, secondly, the hydrogen it produces carries off the nitric oxide that would otherwise lie on the surface of the solution and be absorbed.

Tin and hot concentrated hydrochloric acid do not sensibly destroy hydroxyammonium chloride. This is our experience, and it confirms that of Mr. Shimidzu and one of us, as to the want of action of zinc and sulphuric acid upon hydroxyamine. Further, *stannous chloride in acid solution has no action upon hydroxyammonium chloride*, even when boiled with it; that is, for a reasonable time; an aqueous solution could itself not be boiled very long without suffering some change. Were either tin and hydrochloric acid, or stannous chloride, capable of converting hydroxyamine into ammonia, what we assert concerning the non-production of ammonia from nitric oxide by tin and hydrochloric acid could not, of course, be true. According to v. Dumreicher, however, "at a temperature of 100°, hydroxyamine is quickly and completely reduced to ammonia by excess of stannous chloride" (*loc. cit.*).

Coming now to the use of stannous chloride, our experience is, that with exclusion of air, *not a trace of ammonia is formed by its action upon an acid solution of hydroxyamine*. In working, we prefer to use a mixture of ferrous sulphate, nitric acid, and sulphuric acid as the source of the nitric oxide. It yields the gas in a pure state, and the generator can be charged and worked so as to furnish easily, except for a short time at first, a gentle stream of the gas for 24 hours

at a stretch. To destroy any nitric peroxide, formed through entrance of traces of air into the generator, the gas is sent through a wash-bottle of potassium hydroxide solution. This bottle is scarcely necessary, however, as reaction between ferrous sulphate and the acids does not begin in the cold; and before starting the disengagement of nitric oxide, a current of hydrogen is sent through the whole series of flasks and bottles until all air has been driven out. Only then is the evolution of nitric oxide commenced and passed into the apparatus, the current of hydrogen being at the same time discontinued. The remote end of the arrangement is provided with a wash-bottle as a guard against any reflux of air. When the process is finished, or when it has to be interrupted, the current of nitric oxide is stopped, and its place taken by one of hydrogen again, until all nitric oxide has been chased away. The flasks of tin chloride may then be opened with impunity, air having no effect upon the hydroxyamine already formed, not even when stannous chloride is still present, and being so, goes on changing into the stannic salt by contact with the air.

The reaction between acid stannous chloride and nitric oxide is not quite simple, however. The greater part of the nitric oxide becomes hydroxyammonium chloride, but a part of it is always converted into nitrogen. No nitrous oxide is formed. Since much of the nitric oxide passes unabsorbed, we could not well take the proportions of it to the hydroxyamine formed at the same time. But we many times collected it in quantity, the nitric oxide we were using being tested and found pure, as from its source it was sure to be.

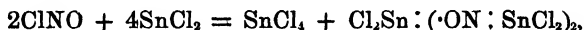
Stannous chloride can be readily and completely, but slowly, changed to stannic chloride by the gas. Some interesting colour-changes are always observable, which serve to indicate the completion of the passage to stannic chloride. They are due, no doubt, to the presence of a trace of iron. Soon after the gas begins to pass, the solution becomes slightly greenish-brown, and so continues until all stannous chloride is used up by the gas: the colour then changes to a faint yellow. If, before all stannous chloride is destroyed, the current of nitric oxide is replaced by one of hydrogen, the solution is bleached; but if all the tin is stannic chloride, the solution does not lose its slight yellow colour by treatment with hydrogen. The yellow colour we suppose to be due to ferric chloride, the brown to the nitric oxide compound with ferrous chloride, the bleaching to the dissociation of this compound by the physical action of the hydrogen. We sometimes succeed in getting hydroxyammonium chloride in quantity equivalent to nine-tenths of the stannous chloride converted to stannic chloride, but generally we get less, at times much less. The reason of this we do not know. We have tried the effect of ferric chloride upon the reaction, and find it to be without noticeable action.

The nitrogen observed seems to us quite sufficient in quantity to account for the stannous salt converted to stannic, over and above that quantity needed for the hydroxyamine.

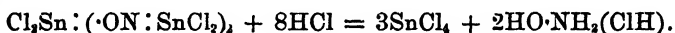
There is a remarkable fact about the reaction between nitric oxide and stannous chloride, we have yet to mention. *At a temperature of fully 100°, there is no action between nitric oxide and acid stannous chloride solution.* The stannous chloride remains unchanged for hours together, and neither nitrogen nor hydroxyamine is formed. The only thing we have noticed is always a trace of ammonia in experiments at 100°, and this, we are inclined to believe, is due to some other cause than this reaction alone. At 90°, the action is still exceedingly small, but as the temperature descends from about 80°, it becomes rapidly greater with the descent.

We have tried cooling the tin-solution by a freezing mixture, but have not succeeded in getting better results than at the ordinary temperature. Further experiments are needed, to be sure that a low temperature does not favour the reaction.

In order that nitric oxide should become hydroxyammonium chloride, it is essential that it should enter into combination with either the stannous chloride or the hydrochloric acid. Of these two, it is much more likely to unite with the former. The following representation seems probable:—



and—



Reaction of Nitric Acid with Hydrochloric Acid and Stannous Chloride.

When nitric acid is in presence of enough water to prevent any reaction taking place between it and hydrochloric acid, it is not perceptibly acted upon by stannous chloride. It may be left for a day or two mixed with these reagents, and remain, as well as the stannous chloride, unchanged. We have not yet established this fact by quantitative estimation, air having been allowed access to the mixture in our experiments hitherto, but we have no reason to believe that it is incorrect.

If such a mixture is sufficiently dilute, it may even be boiled without change, but if not too dilute, reaction is thus set up. Another way of bringing about reaction in such a dilute solution, is to add sulphuric acid, already slightly diluted so that the heating effect of mixing it with water may be avoided, since that alone would afford an explanation of its action. It is thus seen that the addition of

sulphuric acid, by diminishing the weakness of the solution in acid, serves to induce the reaction between the tin salt and the nitric and hydrochloric acids.

When dilute nitric acid added to the solution of stannous chloride in hydrochloric acid is not too dilute, reaction between them proceeds and continues until either the stannous chloride has all become stannic chloride, or until the solution has become too dilute in hydrochloric acid. In the latter case, we believe that we can cause the reaction to go on again, by passing hydrochloric acid gas into the solution, but we have not tried that yet. We have only at present added sulphuric acid as mentioned above with very favourable results. We have not succeeded, however, in destroying all nitric acid.

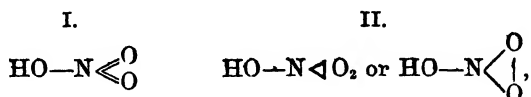
The reaction which takes place results in the conversion of so much of the nitric acid as is decomposed into hydroxyammonium chloride and nothing else—no ammonia and no gaseous body, provided the stannous chloride remains in excess. This statement is in direct opposition to that made by v. Dumreicher,* which is, that “acid stannous chloride acting on nitric acid yields hydroxylamine, but the reaction proceeds further, and the *hydroxylamine is nearly simultaneously reduced to ammonia*.” When the stannous chloride is in insufficient quantity, the conversion of the last portion of it is followed, first, by the solution becoming yellow and smelling of nitrosyl chloride, and then by an effervescence of nitrous oxide. If, on the disappearance of this yellow colour, more stannous chloride is at once added, the solution is at once bleached; and if this additional quantity of stannous chloride is insufficient, the liquid again becomes yellow after a time. The phenomena observed in this case, in fact, strongly remind one of those noticed by Vernon Harcourt, in a solution of hydrogen peroxide and hydrogen iodide to which sodium thiosulphate is added each time coloration by iodine reappears (this Journal, 20, 460). When we proceeded in this way, the solution soon became charged with nitrous oxide, which escaped with effervescence on stirring.

From what we have said, it will, we think, be seen that nitric acid, as such, is not attacked by stannous chloride, the formation of hydroxyamine taking place from a product of the reaction between nitric and hydrochloric acids. Now, the reaction known to occur between these acids yields chlorine and nitrosyl chloride, and the question here needs to be answered, if we are to trace the nature of the production of hydroxyamine, whether these are primary or secondary products of the reaction. Could we answer this question by ascertained facts, we should, we expect, be in a position to throw

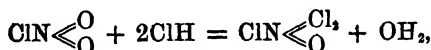
* Abstract of his paper in this Journal.

light on the constitution of nitric acid, as to whether its nitrogen is trivalent or quinquivalent.

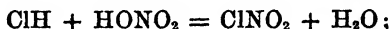
Our work, however, has not yet been carried to such a point. If nitric acid has the constitution I, we see no simple way of



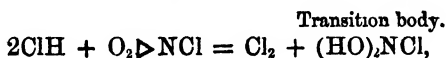
explaining the formation of nitrosyl chloride, for, admitting it to be produced by the splitting up of a transition-body, ONCl_3 , how are we to account for the formation of this body? Why, as in the equation—



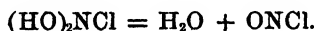
should the hydrochloric acid give its chlorine to nitrogen in exchange for oxygen, when the nitrogen cannot even, *ex hypothesi*, retain this chlorine? But if, as one of us has already suggested in a paper on the constitution of some non-saturated oxygenous salts, formula II is the correct one, a perfectly satisfactory account of the reaction can be given. First, of course, on either view, there is, as a part of the change,—



then follows (nitrogen being trivalent), in consequence of the powerful oxidising property of nitroxyl chloride,



and lastly,—



We, therefore, until further investigations have been made, hold the opinion, that the reaction between nitric acid and hydrochloric acid does not produce some as yet unknown substance, having its nitrogen quinquivalent, which is then converted by stannous chloride to hydroxyammonium chloride, but that nitrosyl chloride and chlorine are produced, as established by Tilden. There will, then, be the chlorine uniting with one part of the stannous chloride, and the nitrosyl chloride uniting—both nitrosyl and chlorine, with more stannous chloride. Finally, the nitrosyl compound with stannous chloride will react with hydrochloric acid, as already described of nitric oxide.

If we can succeed in converting all the nitric acid into hydroxyammonium chloride, this method will probably be found very

satisfactory for preparing this salt readily, and free from ammonium chloride. There is a chance of succeeding by passing hydrochloric acid gas into the solution, a method which, as we have said, remains yet for us to try.

In our next communication, we hope to be able to report on this point—as also on the reaction of stannous chloride with nitrites, nitric peroxide, nitrosyl sulphate, ethyl nitrate, and other compounds.

Stannous sulphate lying in dilute sulphuric acid has not yet given us either ammonia or hydroxyamine with nitric oxide, air and hydrochloric acid being both excluded. The stannous sulphate is slowly oxidised, and we suppose that it converts the nitric oxide to nitrogen, but this we have not yet tested. Neither have we succeeded in getting hydroxyamine by the action of stannous sulphate upon nitric acid. Longi has lately published a volumetric method of estimating nitric acid by means of stannous sulphate and a little hydrochloric acid. We have not ourselves proceeded to a full examination of the reaction.

When a mixture of nitric and hydrochloric acids acts upon metallic tin, ammonia is formed as well as hydroxyamine. But ammonia is always formed when nitric acid alone acts upon tin, and in accordance with what is stated in the paper "On the Specific Action of mixed Sulphuric and Nitric Acids upon Zinc," we consider that two actions proceed at once—one being the direct action of the nitric acid on the tin, giving rise to ammonia and oxides of nitrogen; the other being the specific action of nitro-hydrochloric acid on the tin, giving rise, not to ammonia, but to hydroxyamine. The formation of ammonia, as well as hydroxyamine, when ethyl nitrate is used, as in Lossen's original method, is, no doubt, due also to the action of the metal upon the ethyl nitrate or nitric acid derived from it. We are confident that stannous chloride will produce no ammonia from ethyl nitrate, although we have not yet tried it. Von Dumreicher has got a yield of 90 per cent. hydroxyamine from ethyl nitrate by means of stannous chloride, but he makes no mention of ammonia not having been produced (judging, that is, from the abstract of his paper in this Journal).

We may here call attention to the facts, that whilst metallic iron always forms ammonia from nitric acid, whether another acid is present or not, ferrous salts produce nitric oxide and no ammonia, so distinct is the action of a metal from that of its reducing salts.

In a paper "On the Production of Hydroxylamine from Nitric Acid," one of us has described an experiment in which even more than 80 per cent. of nitric acid was converted to hydroxyamine by means of tin and a concentrated solution of hydrochloric acid. With the

help of Mr. Shimidzu, that experiment has been repeated, and has again given 80 per cent. of the nitric acid as hydroxyamine.

In the paper referred to in the preceding paragraph, the production of hydroxyamine by means of aluminium was described, and the peculiarity pointed out that hydroxyamine is only found when the hydrochloric and nitric acids have been for some time in action upon the metal. It was there also suggested that the presence of aluminium chloride might therefore be an important factor in this production of hydroxyamine. Since that paper was published, one of us, with the assistance of Mr. T. Shimidzu, has tried the effect of having much aluminium chloride with the mixed acids when they are poured upon the metal, and found this salt to exert no apparent influence upon the production of hydroxyamine. The peculiarity referred to—that of the lateness of the production of this substance, must, therefore, be due to some other circumstance, such as the change in activity towards the acids which the aluminium certainly experiences in the course of its dissolution.

LXVI.—*On the Constitution and Reactions of Liquid Nitric Peroxide.*

By EDWARD DIVERS, M.D., and TETSUKICHI SHIMIDZU, M.E.

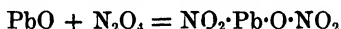
THERE are only two constitutional formulæ for liquid nitric peroxide that have sufficient likelihood of being true to need consideration. The one represents it as formed by the union of the nitrogens of two molecules of the peroxide as it exists at high temperatures, $O_2N \cdot NO_2$. The other represents it as nitrosyl nitrate (Odling), $ON \cdot O \cdot NO_2$ or $(NO)NO_3$.

In favour of the first formula may be advanced its symmetrical character, and the probability that in combining, the two NO_2 -groups will unite symmetrically. Against it is the fact, that when two nitrogen-atoms have once united, they do not readily separate again, as is seen in nitrogen itself, nitrous oxide, diazo-compounds, and the hydrazines.

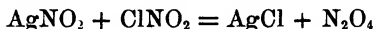
In favour of the latter formula, there is the reaction of the peroxide with water and alkalis, by which nitrite and nitrate are formed. We question, however, whether this reaction takes place in the simple manner supposed, and intend, indeed, to test the matter experimentally. It is quite likely that the reaction



the nitric oxide then forming, in presence of a base, a nitrite at the surface of the liquid with the assistance of the oxygen in the air. If, however, it can be shown, that in absence of all free oxygen nitric peroxide forms, with alkalis, nitrate and nitrite in molecular proportions, this will still be insufficient to prove that it is nitrosyl nitrate. Its action upon alkali may well be similar to that of chlorine, half of it taking metal, the other taking metaloxyl:—

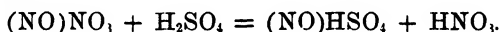


Exner has suggested that the reaction he observed as taking place between silver nitrite and nitroxyl chloride,



(this Journal, 25, 1072), was in favour of the constitution of the peroxide being nitrosyl nitrate. But this reaction only favours this view so long as nitrites are treated as oxylic salts, AgONO . When they are regarded as haloid salts, $\text{Ag} \cdot \text{NO}_2$, it no longer does so.* The silver and chlorine unite together and leave one NO_2 to unite with the other as usual.

The reaction of the peroxide with sulphuric acid, as described by Lunge, is the only evidence that has yet been given of the peroxide being nitrosyl nitrate. In that reaction it forms nitrosyl sulphate and nitric acid—

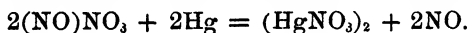


We think that facts recently ascertained by us, will be admitted to go far in assisting to determine the constitution of liquid nitric peroxide.

Action of Nitric Peroxide upon Mercury.—Rectified nitric peroxide was used, contained in sealed tubes, which were broken at the point when the contents were wanted. It was added to the mercury in a tube filled with dried carbon dioxide. The tube containing the two

* *Note by Edward Divers.*—I may be permitted to point out that in the discussion of my paper "On the Constitution of some Non-saturated Oxygenous Salts" (no doubt in consequence of its having been necessarily only read in abstract), it was a mistake to represent me as basing any part of my argument, as to the constitution of nitrites, upon such slight decomposition as takes place between silver nitrite (also silver sulphite) and phosphorus oxychloride. That action I recorded as an experimental fact, at the same time expressing my belief that it had only occurred in consequence of the presence of a trace of moisture. The action will then, of course, have been $6\text{AgNO}_2 + \text{OPCl}_3 = 3\text{AgCl} + \text{OP}(\text{OAg})_3 + 3\text{N}_2\text{O}_3$. It could hardly have been anything else, and it has no value as evidence on the point in question. My argument was simply this: nitrites do not produce nitrosyl chloride with oxychloride of phosphorus; if they did, the fact would be a convincing proof of their oxylic constitution, whilst that they do not must cast doubt upon the truth of this view of their constitution.

liquids was sealed and left for an hour or so. The supernatant has peroxide had then become faintly green only, the mercury had become tarnished and pasty, and on opening the tube, a little action oxide escaped. The mercury was gradually converted into a mass, sending out, in some experiments, slender branches with little globules of mercury borne on their points. Nitric oxide was continuously evolved, and the residual peroxide became olive-green. The white salt was gently warmed in a current of carbon dioxide for some time to evaporate unchanged peroxide. It was hard, and adhered firmly to the glass. Removed and ground to powder, it was found still to contain a little liquid peroxide. Tested, it proved to be mercurous nitrate, with some mercuric nitrate, but no nitrite. Tested by ferrous sulphate and by potassium iodide, only slight coloration was obtained, attributable to traces of nitric peroxide, which for some time adhered to it, in spite of exposure to air. In one experiment, in which both the mercury and the product of the action were weighed, but in which a very little metal remained in excess, the increase was found to be slightly greater than calculation for mercurous nitrate required, the excess in weight being, no doubt, caused by the mercuric nitrate found to be present. The reaction must have been, therefore, the replacement of nitrosyl by mercury—



Action of Nitric Peroxide upon Silver.—Reduced spongy silver was used. It was sealed up with the peroxide in an atmosphere of carbon dioxide. The reaction proceeded very slowly. Nitric oxide was evolved, the excess of nitric peroxide became olive-green, but the silver did not appear to be much changed, even after several days' contact. This, however, seems to be due to the whiteness of the metal, which renders a thin coating of a white salt almost invisible, as an action did take place. The excess of peroxide, poured off from the silver and evaporated by itself, left no residue of silver salt. After drying the silver in a current of carbon dioxide, it was treated with water. This dissolved a considerable quantity of silver salt, although most of the metal had remained unattacked. The salt was nitrate, without admixture of nitrite. In the case of mercury, the action went on to the end in spite of the insolubility of the nitrate in the peroxide, because of the mobility of the metal, whilst in the case of silver, the solid metal became coated with nitrate, and the action was thus arrested. Nevertheless, we meet again with a reaction, which is the replacement of nitrosyl by the metal, and the conversion of nitrosyl nitrate into metal nitrate.*

* Berthelot and Ogier (*Compt. rend.*, 96, 30) speak of an action of "nitrous acid" upon hot silver in describing their experiments upon silver hyponitrite.

the action of Nitric Peroxide upon Copper.—Reduced spongy copper surfaced with nitric peroxide, in the same way as mercury and howe had been treated. Immediately on contact there was considerable action; brisk effervescence, through escape of nitric oxide, occurred at first and gradually lessened, and the copper turned grey, with a bluish or greenish tinge. The excess of peroxide became of an intense deep-green colour, unlike the dull olive-green in the mercury and silver experiments. This green liquid, decanted and partly evaporated, lost its green colour, and when the peroxide had all volatilised, nothing was left, so that the green colour was not due to dissolved copper salt. We are unable to explain the difference between copper and the other metals, in producing this colour. It was always observable. Perhaps the rapidity of the formation of nitric oxide by the copper had something to do with it. We should mention that the evolution of gas being so great, the point of the tube could not be sealed, as it had been in the experiments with the other metals, until action had considerably lessened. The green solution was, therefore, not due to any pressure upon the gas. In the mercury and silver experiments, in which the reaction takes place at the ordinary temperature, it is not strange that the nitric oxide should not combine with, or dissolve in (Armstrong) the nitric peroxide, to form the blue liquid which is produced at low temperatures.

Long digestion of the copper with the nitric peroxide did not seem to add much to the extent of the action, which at first proceeded so briskly. In one experiment, the copper was found to have taken up a fifth of its weight, but then the change of the copper is only on its surface. We believe the product of the reaction to be cuprous nitrate, mixed with a little cupric nitrate. Cuprous oxy-salts hardly exist, it is true, but we have here the absence of water as perhaps the reason why such a salt may be produced. Ground to fine powder and very gently warmed, so as to expel adhering nitric peroxide, it shows the following reactions. Aqueous vapour changes its colour to a red-brown; water at once changes it to a bright copper colour, evidently by formation of free copper. At the same time, the water becomes blue from the presence of cupric nitrate. This action of water, we interpret to be the decomposition of the grey cuprous nitrate into metallic copper and cupric nitrate. The action of water at once sets up an effervescence of nitric oxide from the copper, and basic copper nitrate is slowly produced. This action we regard as being one between finely divided—spongy and freshly precipitated—copper and cupric nitrate. If the first water is decanted, and the copper is washed, the latter no longer effervesces with water, but if the first blue-coloured solution be now poured back on the copper,

effervescence begins again. Strong potassium hydroxide solution precipitates cuprous hydroxide with some cupric hydroxide, and leaves an azure-blue mother-liquor. Weaker alkali gives less cuprous hydroxide, and a free effervescence of nitric oxide. Strong sulphuric acid has no apparent effect, but the diluted acid acts much like water. On rendering the solution alkaline, an azure-blue mother-liquor is obtained. From the above reactions, it would seem that ammonia is formed during the decomposition of the substance by alkalis and acids. The filtered alkaline solution, obtained by treating the substance with potassium hydroxide, yields the reactions of nitrite to a small extent. But, since cuprous hydroxide seems in this case to have a reducing action upon the nitrate, producing ammonia and nitric oxide, this nitrite may be regarded as a secondary product.

The reaction of nitric peroxide with copper is of too uncertain a nature to throw light upon the constitution of the peroxide, at least until we know more about it.

Action of Nitric Peroxide upon Silver Nitrite.—Dry silver nitrite may be digested for days with nitric peroxide, and the latter may be repeatedly distilled off it, without its being oxidised, or in any way changed. This is a fact of importance in studying the effect of heat on silver nitrite, by which both nitric peroxide and silver nitrate are formed.

Action of Heat upon Silver Nitrite, Air being excluded.

By heating silver nitrite, Péligot obtained silver, nitric peroxide, and silver nitrate. One of us also re-investigated the effects of heat upon silver nitrite 14 years ago, and communicated an account of the results obtained to this Society. It was there shown that, by modifications in the way of heating, the products could be made to vary, nearly from nitric peroxide and silver only, to nitric oxide, silver, and silver nitrate. It was also proved that oxygen is absorbed from the air, and that nitric oxide acts as the carrier of this to form nitrate.

In that paper, it was assumed that the nitrate was formed by the oxidising action of the peroxide upon the nitrite. This assumption we now consider to be wrong, for reasons which we shall give after describing our recent experiments with silver nitrite. The object of these experiments was to test the effect of heating silver nitrite when not in contact with air.

Out of a piece of tubing, not more than 1 cm. in diameter, we constructed a horizontal retort with a receiver and gas-exit tube for connection with a Sprengel pump. After charging the retort with dried silver nitrite, its mouth was sealed off, the gas tube connected with the pump, and the apparatus exhausted, both retort and receiver being

kept gently heated for some time to expel moisture. The receiver was then put into a mixture of ice and salt, and the flow of mercury stopped. The retort was next heated, by a large spirit flame, as rapidly as possible, and the nitrite thus decomposed in less than a minute. Much nitric peroxide condensed in the receiver, besides an abundant fume of silver nitrate, and the nitric oxide escaped at the exit-tube. Very little silver nitrate was carried over mechanically. The nitric peroxide had only a slight green colour, showing how easily, at a low temperature, nitric peroxide and nitric oxide may exist together without combining, and thus favouring Armstrong's belief in the non-existence of nitroysl oxide. Proceeding in this way, and weighing our nitric peroxide, we found it to represent not much less than two-thirds of the nitrogen of the nitrite, the rest of the nitrogen having become nitrate and nitric oxide. In the paper referred to, experiments are given in which the metallic silver obtained represented a much nearer approach to the production of only nitric peroxide and silver, but those experiments were conducted in hot air laden with steam. The mercury of the trough was only acted upon to a small extent, proving that very little nitric peroxide escaped with the relatively small volume of nitric oxide produced.

In another experiment, and in an apparatus very similar to that just described, silver nitrite was kept heated at 125° in absence of air for 15 hours, when gas had almost entirely ceased to come off. The mercury was considerably soiled by the gas, showing that nitric peroxide had been given off, but no liquid peroxide was ever condensed in the receiver, and very little red vapour was ever visible. In this way, nearly half the nitrite was converted to nitrate, as calculation requires, and the results in the paper referred to were thus confirmed.

We can now give our reasons for believing that the formation of silver nitrate is due to reaction between silver and nitric peroxide, and not between nitrite and the peroxide.

(1.) We have found, as already described in this paper, that nitric peroxide does act upon silver, and then forms nitrate and nitric oxide. (2.) We have found that nitric peroxide does not act upon silver nitrite in the least, even after prolonged contact. (3.) One of us has found that when silver nitrite was heated for 78 hours at a temperature slowly raised from 90° to 136° during that time, in an apparatus which allowed of the exit of gases and entrance of air occurring only through the space between the walls of a tube and a glass rod almost filling it, only a small fraction of the silver was obtained as metal, most of the nitrite having become a stable mixture or compound of nitrate and unchanged nitrite in molecular proportions. Now, whilst the conversion of nearly all even of the silver nitrite to nitrate, would in itself be consistent with either supposi-

tion, the fact that so little metallic silver was found seems to indicate that the nitrate had been formed from the metal, and not directly from the nitrite. For if it had been the nitrite which was oxidising during the 78 hours' heating at $90-136^{\circ}$, then silver ought to have gone on increasing, as an effect of the continued action of heat upon silver nitrite, instead of being finally only $4\frac{1}{2}$ per cent. of the whole silver, or $8\frac{1}{2}$ per cent. of the silver of the changed nitrite. That it formed only this small proportion is due, we consider, to the silver being converted to nitrate nearly as fast as it was liberated from the nitrite. (4.) Facts seem to show that nitrites are non-oxylic salts, having, therefore, the metal united directly with the nitrogen. This is now widely admitted to be so in the case of silver nitrite, at any rate. On upholding this view of the constitution of nitrites in a recent paper to the Society, one of us has pointed out that it is apparently the metal radical which is oxidised when oxidation takes place. The conversion of nitrite to nitrate, on this view, involves the oxidation of the metal, and it seems improbable to us that silver and nitrogen in nitrite part from each other to take in oxygen. At least, silver sulphide does not oxidise to silver sulphate, but readily changes with hot water to silver itself and sulphuric acid, and in an experiment given in a paper by one of us already referred to, most of the silver of the silver nitrite was got in the metallic state by the action of hot air and steam. These are our reasons for believing that the nitrate formed, when silver nitrite is heated, comes not from the oxidation of the nitrite, but from a reaction between silver and nitric peroxide (nitrosyl nitrate).

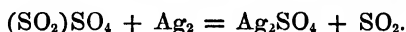
LXVII.—*On the Action of Pyrosulphuric Acid upon Certain Metals.*

By EDWARD DIVERS, M.D., and TETSUKICHI SHIMIDZU, M.E.

ALTHOUGH the molecule of gaseous sulphur trioxide is expressed by SO_3 , there are grounds for regarding the liquid or solid trioxide as having a molecule at least twice as great. The conversion of the trioxide by phosphorus pentachloride into $\text{S}_2\text{O}_6\text{Cl}_2$, and not SO_2Cl_2 , has already been adduced by Michäelis as evidence that the trioxide is S_2O_6 . In a recent paper, already received by this Society from one of us,* this doubling of the formula has also been advocated. It

* Divers "On the Constitution of some Non-saturated Oxygenous Salts" (this vol., p. 205).

is there pointed out, that the action of hot undiluted sulphuric acid upon mercury, silver, and copper, may best be regarded as a reaction between these metals and sulphur trioxide, into which substance and water, sulphuric acid begins to dissociate at a comparatively low temperature. At comparatively low temperatures, also, the action of sulphuric acid on these metals begins, and, like the dissociation of the acid, increases as the temperature rises. According to this view, the reaction is, then, to be represented as the displacement by the metal of sulphuryl from its sulphate, thus:—



This representation is in entire accordance with what is known of the properties of the substances concerned, while the only other view of the reaction that has been advanced, namely, that in which the silver or mercury is represented as displacing hydrogen, is without the support of any evidence of the capability of such metals to displace hydrogen from any oxylic compound.

The view advanced in the paper referred to, we are now in a position to support by experiments which appear to leave no room for doubt as to its being the true one.

Mercury, silver, and copper are all unacted upon by sulphur trioxide, provided moisture is rigorously excluded. With this rigid exclusion of moisture, the only phenomenon observable is the ready pulverisation of the mercury, when it is shaken with the trioxide, but even after contact for days, no evidence of chemical change is obtained. The case is otherwise when a little moisture, a very little sulphuric acid, that is, is present.

Reduced spongy silver dropped into pyrosulphuric acid warmed barely to its melting point, gives a momentary hissing and effervescence, the cause of which is not quite clear, but may well be gases condensed and moisture in the pores of the silver. The metal now dissolves rapidly in the liquid, without the least further effervescence. Its solution is much denser and more refractive than the acid, and is thus easily distinguishable from it. Its rapid dissolution is attended with marked rise in temperature, so that external cooling must be applied in order to see the change proceeding in the cold. This cooling does not induce recrystallisation of the acid, partly because it has become weaker by the action, and partly because of the continued generation of heat within it. Its solution when poured into water deposits silver sulphate, and charges the water with sulphur dioxide.

Mercury poured into pyrosulphuric acid behaves very like silver, except that the first contact is not attended, for some time, with any effervescence, provided that the vessel is shaken occasionally to renew contact. As the action proceeds, mercurous sulphate slowly

separates in the solid state. By using an acid containing much sulphur trioxide, the whole may become solid, and the action be arrested in consequence. In any case, when the action has proceeded far, sulphur dioxide escapes freely from the liquid with slight effervescence. If the solution of the mercury in the acid is poured into water, mercurous sulphate is precipitated, mixed with metallic mercury, and no sulphur dioxide is left. But the already solidified mercurous sulphate is not thus affected by contact with water.

The dissolution of silver and mercury without evolution of gas, at least for a time, is a phenomenon due to the very great solubility of sulphur dioxide in fuming sulphuric acid. Even oil of vitriol dissolves, according to Kolb, nearly six times its volume of sulphur dioxide.*

The precipitation of metallic mercury, observed when the fuming acid solution of mercury salt is poured into water, is nothing but the effect of the known action of sulphur dioxide upon mercurous salts.

Coming now to the reaction itself, in which silver and mercury so very readily dissolve in the cold acid, this will be seen to be just what takes place at a high temperature with oil of vitriol, and then, indeed, no more freely than here in the cold. That the reaction, when taking place in the fuming acid, is, as we have represented it to be, a reaction between the trioxide and the metal, and not one between the acid (hydrogen sulphate) and the metal, can hardly be denied. If hydrogen sulphate is the real agent in dissolving the metal, then it is certainly difficult to see why it should fail to act when it is in the state of oil of vitriol. That the fuming acid should act where the anhydrous trioxide fails to do so, admits of simple explanation, as being a consequence of the necessity of some solvent for the products, such as is afforded by the sulphuric acid.

But, if further evidence be needed, it will be found in the behaviour of copper with pyrosulphuric acid. In the first place, copper sulphate is well known to be practically insoluble in cold concentrated sulphuric acid, whereas silver sulphate is very soluble, and mercurous sulphate somewhat so. In the second place, as Pickering has established, within certain limits, the lower the temperature at which ordinary sulphuric acid acts upon copper the more nearly does the reaction approach that in which nothing but copper sulphate and sulphide are the products (besides water):—

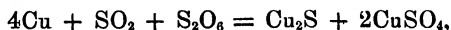


Now, when spongy copper, reduced in hydrogen, is put into fuming sulphuric acid, there is slight effervescence as in the case of spongy

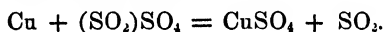
* *Lunge's Sulphuric Acid.* Lunge has corrected Kolb's table as published, and we refer to the corrected number.

silver, but the copper soon blackens, and then further action appears to proceed with extreme slowness. Only traces of copper salt are to be found in the acid liquid. The blackened copper dropped into water gives up some sulphate to it, but retains its black coating. On now moistening it with nitric acid, sulphur is liberated as the black coating is dissolved.

Here then, quite in the cold, the above reaction has occurred quickly enough while it lasted, although soon arrested by the insolubility of the products in the cold acid. As pointed out in the paper referred to, Pickering's reaction is to be attributed—taking into consideration the reaction of sulphur trioxide with stannous chloride and many other oxidisable substances—to a decomposition of sulphur dioxide by copper—



this reaction following and being intimately associated with that of the copper upon the sulphur trioxide:—



If tin is digested for some time with warm pyrosulphuric acid, the acid becomes coloured an intense indigo-blue, the metal to a slight extent being converted to insoluble stannous sulphate. The blue colour, which is immediately destroyed by water with liberation of sulphur, is caused by sulphur sesquioxide. The formation of this sulphur serves to show that sulphur dioxide (at any rate, trioxide) is reduced to sulphur and oxygen, the sulphur here not being able to form tin sulphide, because of the presence of the fuming sulphuric acid.

Note on the Preparation of Mercurous Sulphate.

Mercurous sulphate, in special demand for the Latimer-Clark cell, is somewhat troublesome to prepare free from mercuric salt, by heating mercury with sulphuric acid. We wish, therefore, to point out that it can be prepared in the cold, by leaving together mercury and fuming sulphuric acid rich in trioxide, the only care necessary being to keep the vessel covered and cooled. When the metal has all disappeared, the uncovered vessel may be left in a warm place to expel the last portions of sulphur dioxide. It is evidently desirable to so apportion the acid as to have as little of the trioxide left unconsumed as possible, so that where the mercury taken has proved much too small, more had better be added, still avoiding excess. The product needs only to be transferred to water and washed to be ready for use.

LXVIII.—*A Method for Obtaining Constant Temperatures.*

By Professor WILLIAM RAMSAY, Ph.D., and SYDNEY YOUNG, D.Sc.,
Lecturer and Demonstrator of Chemistry, University College,
Bristol.

THE physicist and chemist often require to raise apparatus to a known temperature higher than that of the air, and to be able to vary such temperature at will, keeping it constant, if desired, for any length of time. Various devices have been used for this purpose, among which may be mentioned divers forms of water-baths, air-baths and oil-baths heated by flames the heights of which can be so regulated by thermostats as to ensure an approximately constant temperature. But all such arrangements are defective: it is impossible to avoid convection currents, even by vigorous stirring; rapid alteration of temperature is impossible, and it is a difficult and tedious operation to obtain a definite temperature.

The temperature of the vapour of a pure substance boiling under a constant pressure is practically constant throughout, the pressure of the column of vapour itself being a negligible amount; and vapours are frequently employed as heating agents, as, for example, in Hofmann's method of determining vapour-densities. But although this device is greatly superior to those already alluded to, in so far as the temperature is a constant one so long as the atmospheric pressure does not alter during the experiment, the number of liquids which are obtainable in a pure state at a reasonable cost is small, and the temperatures which can be reached by this method are at somewhat wide intervals.

It is possible, however, to alter the boiling points of such liquids by altering the pressure to which they are exposed. Their vapours then assume temperatures corresponding to the altered pressures; and as the alteration of pressure is an easy matter, complete control over temperature is to be obtained in this manner.

Liquids to be used thus must be of moderate cost; they must be easily obtained pure; they must be stable, so as not to decompose after long ebullition; and their vapour-pressures must have been determined with the greatest accuracy.

We have had occasion to make use of this means of securing accurately known temperatures; and in the hope that it may prove of equal service to others as it has to us, we publish an account of experiments made to determine the vapour-pressures of the liquids employed.

These liquids were: Carbon bisulphide, ethyl alcohol, chlorobenzene, bromobenzene, aniline, methyl salicylate, bromonaphthalene, and mercury. Their approximate boiling points are 46° , 78° , 132° , 155° , 184° , 222° , 280° , and 358° . By their use any desired temperature between that of the atmosphere and 360° may easily be obtained. These liquids also fulfil the required conditions as regards cost, purity and stability.

It is here advisable to direct attention to another advantage attending this method. The pressure is still high at which the temperature of any one of these liquids is reduced to that of the boiling point, under normal pressure, of the one next lower on the list, and a considerable alteration of pressure may be made without altering the boiling point perceptibly. Hence an alteration of temperature of one-tenth of a degree can usually be carried out with certainty. For example, the boiling point of bromobenzene under a pressure of 750.7 mm. is 155.64° . At that temperature the pressure of aniline-vapour is 337 mm., and an alteration of 1° corresponds with an alteration of pressure of 10.5 mm. As it is possible to alter the pressure by half a millimetre with perfect ease, it is evident that the temperature could be altered 0.05° by such a change.

Careful determinations of the vapour-pressures of these substances have been made. Those of carbon bisulphide, alcohol and mercury have been determined by Regnault, and his results will be quoted in the tables which follow. The vapour-pressures of the other substances were determined by us by the method described in the *Philosophical Transactions*, 1884, p. 37. A few points on the curves representing relation of pressure and temperature were determined by other methods for the purpose of reducing the readings of a mercurial, to those of an air thermometer.

As we have endeavoured to arrive at the utmost accuracy, seeing that much of our work has depended on these results, we shall discuss separately the data obtained with each substance.

The thermometers used in the preliminary determinations were of German soda-glass. They were carefully calibrated by the method of separating a single column, and the zero point and the boiling point of water were frequently redetermined during the research. For temperatures above 140° , air was introduced in order to prevent volatilisation of mercury. As the stem was always heated to the same temperature as the bulb, no correction for the expansion of the mercury in the stem was required. These readings show the general form of the curve, and may be regarded as very nearly accurate for the temperatures registered by the thermometers used. The pressures are corrected to 0° :—

I. *Chlorobenzene.*

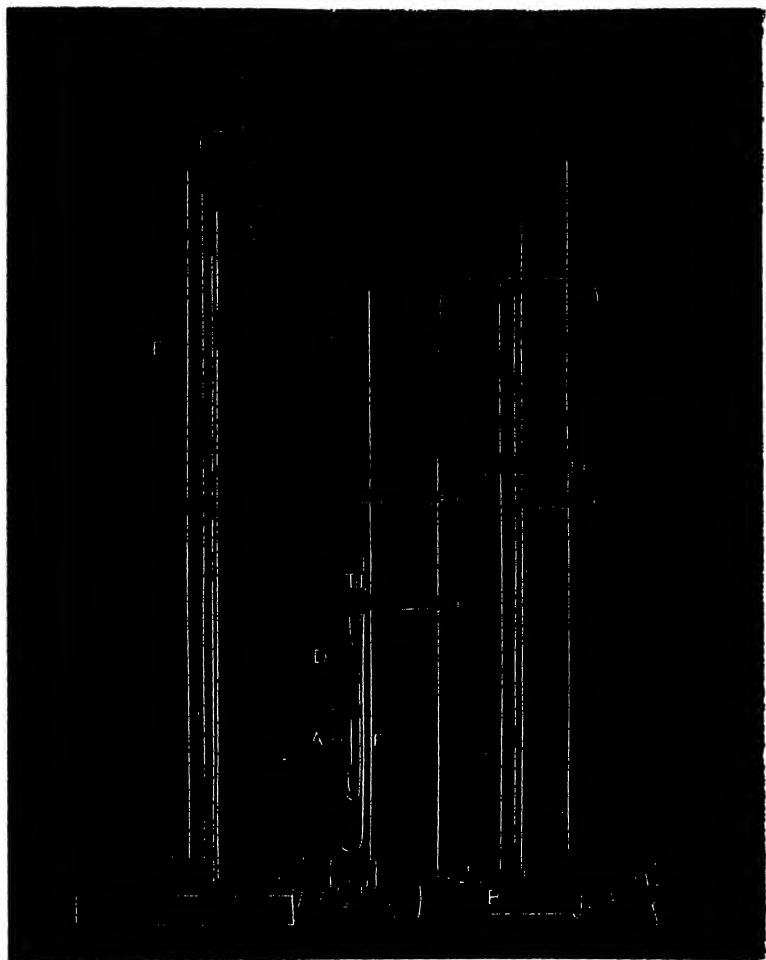
T.	P.	T.	P.	T.	P.
	mm.		mm.		mm.
26°·2	11·95	71°·6	103·1	105°·2	345·6
29·2	14·1	72·0	107·1	108·2	350·8
34·6	18·4	77·2	129·5	109·2	393·3
36·1	20·15	77·2	130·0	113·6	448·3
44·0	30·2	82·3	160·3	116·3	486·5
45·2	33·4	84·2	168·55	117·9	505·7
50·2	40·3	86·3	181·3	121·2	556·2
53·0	47·55	90·3	212·3	123·4	599·9
53·5	48·05	92·7	226·0	124·2	611·2
58·2	57·2	94·2	241·2	128·2	688·7
58·9	61·35	96·4	255·5	128·3	685·7
59·5	63·95	97·7	269·3	131·7	756·0
64·2	74·9	100·2	296·2		
65·3	80·75	101·3	307·9		

These numbers were then plotted on curve paper, and a curve was drawn showing the relationship between temperature and pressure. This curve smooths the irregularities of individual observations.

Determinations of the temperature of the vapour of chlorobenzene boiling under different pressures were then made at certain definite temperatures by means of an air thermometer. This thermometer consisted of an air reservoir, A, the capacity of which had been determined accurately to a mark on the stem, by weighing it full of mercury at a known temperature. The stem itself was calibrated, so that the volume of air contained in 1 mm. length was accurately known. It was possible, by means of the air-pump B, to alter the pressure on the air in the air thermometer, and so to alter the position of the column of mercury which confined the air in A. This alteration of pressure was shown by reading the differential manometer E, by means of a mirror scale placed behind it. It was thus possible to alter to a small extent the volume of air in A; the amount of this alteration, as well as the difference of pressure, could be read on the mirror scale placed behind A. The substance of which the vapour-pressure was required was placed in the bulb of the jacket D, and pressure could be reduced to any desired amount by means of a pump (not shown in the figure), and the exact value of the reduction of pressure read on the gauge and barometer C, which were also backed by a mirror scale. Keeping the pressure, as shown by C, constant, it was thus possible to obtain different determinations of the product of pressure of air in the air thermometer into its volume, and so, by several readings, to control the results. It may be pointed out here

that the readings of pressure were all reduced to 0° by means of the formula

$$H_0 = \frac{H_t}{1 + 0.000181t}.$$



As the temperature of the column of mercury enclosing the air in A was known from the previous determinations to within at least 1° , and as the temperatures of the gauges were taken as the same as that of the thermometers hung beside them, the reduction was accurately effected: the temperature of all parts of the mercury columns indicating pressure was known with sufficient accuracy.

The air in the air bulb necessarily became saturated with mercury-vapour, and the value of this vapour-pressure, deduced from Regnault's observations, was always subtracted from the total pressure read, before multiplying pressure by volume. Correction was also applied for the expansion of the air reservoir by heat; the coefficient of cubical expansion for the glass used was 0.0000257.

In order to show the accuracy of these observations, we think it desirable to give full details.

1. Capacity of bulb of air thermometer to zero point, 15.190 c.c.
2. Volume of 1 mm. of tube 0.011896 c.c.
3. Volume read $(15.190 + 0.011896 \times l)\{1 + (0.0000257t)\}$; (l , length of stem from zero mark to surface of mercury).
4. Pressure = $B + C + (h_1 - h_2) - \text{Hg}_t$. (B , barometric height at 0° ; b , pressure indicated by differential gauge E at 0° ; h_1 , height of mercury in open limb of air thermometer; h_2 , height of mercury in the limb connected with the bulb; Hg_t , vapour-pressure of mercury at temperature t).

The temperature t was read on a carefully calibrated thermometer by Negretti and Zambra. As it was found impossible to obtain readings when the air thermometer was jacketed with steam, owing to condensation of drops on the side of the jacket, the thermometer by Negretti and Zambra was placed in the usual form of steam jacket, and the boiling point determined. This thermometer was then immediately transferred to the apparatus, and placed in close contact with the air thermometer, the vapour of chlorobenzene being used as a jacket. Pressure was reduced until the thermometer gave the same reading as in steam at 760 mm. pressure, and the following readings of the air thermometer were taken ($t = 100^\circ$):—

B_0 .	$(h_1 - h_2)_0$	b_0 .	Hg_{100} .	P.	Zero mark.	h_2 .	l .	V.	P.V.
758.5	- 7.65	249.75	0.75	999.85	478.2	495.6	17.4	15.434	15,431
758.8	+ 12.75	222.05	"	992.85	"	506.1	27.9	15.558	15,447
"	12.0	221.85	"	991.9	"	505.5	27.3	15.551	15,425
"	31.45	196.15	"	985.65	"	515.5	37.3	15.670	15,446
759.1	54.2	163.80	"	976.35	"	527.3	49.1	15.811	15,437
"	79.35	129.10	"	966.9	"	540.0	61.8	15.963	15,435
759.35	127.1	64.05	"	949.85	"	564.5	86.3	16.255	15,440
Mean..									15,437

From the mean result, the product of pressure into volume at 0° ($P_0 V_0$), was calculated on the assumption that the coefficient of expansion of dry air is 0.003663.

$$P_0V_0 = \frac{P_{100}V_{100} \times 273}{273 + 100} = 11,298.$$

From the value of P_0V_0 the subsequent temperatures were calculated according to the formula

$$273 + t = \frac{P_tV_t \times 273}{11,298}.$$

We think it unnecessary to give detailed results in every case, as the method has been sufficiently shown in the above examples; in order, however, that an opinion may be formed as to the correctness of the results, we give in each case the individual values of P and V ; and, as it may be deemed advisable by those using our results to employ a different coefficient of expansion for air, and to modify the numbers obtained from Regnault's determinations of the vapour-pressures of mercury at the temperatures used, we append the latter numbers.

T. (mercurial).	P. (Chloro- benzene vapour).	P.	V.	P. V.	Mean P. V.	Hg.	T. (air).
	mm.	mm.					°
90	208.4	982.4	15.288	15,019	—	0.5	—
"	"	974.0	15.427	15,026	15,022	"	90
100	295.7	Already given.			15,437	0.75	100
110	400.0	1021.85	15.506	15,845	—	1.00	—
"	"	998.45	15.869	15,845	—	"	—
"	"	989.55	16.005	15,838	15,843	"	109.82
120	540.9	1049.1	15.503	16,264	—	1.50	—
"	"	1039.75	15.657	16,279	—	"	—
"	"	1028.65	15.825	16,278	—	"	—
"	"	1016.75	16.001	16,269	—	"	—
"	"	998.85	16.280	16,262	—	"	—
"	"	1047.45	15.516	16,252	16,267	"	120.06
B. p. under	750.6	1095.55	15.264	16,723	—	2.2	—
atmospheric	"	1080.65	15.499	16,748	—	"	—
pressure	"	1031.3	16.228	16,736	16,736	"	131.39
do.	753.85	1087.45	15.400	16,747	—	"	—
"	to	1080.45	15.507	16,755	—	"	—
"	754.7	1068.4	15.672	16,744	—	"	—
"	—	1042.35	16.071	16,752	—	"	—
"	—	1029.65	16.261	16,743	—	"	—
"	—	1069.0	15.671	16,753	—	"	—
"	—	1026.1	16.337	16,764	16,751	"	131.75
"	759.35	1097.0	15.276	16,758	—	"	—
"	to	1087.05	15.407	16,748	—	"	—
"	759.6	1072.95	15.606	16,744	—	"	—
		1057.9	15.848	16,765	—	"	—
		1046.8	16.004	16,753	—	"	—
		1026.05	16.330	16,756	16,754	"	131.83

These temperatures, although not quite identical throughout with

those registered by Negretti and Zambra's thermometer, were nevertheless identical with those previously obtained with the German thermometer, the difference probably depending on the nature of the glass; hence the curve representing the relations of temperature and pressure with chlorobenzene required no alteration.

The curve was then smoothed by the method of differences. The final results are as follows :—

T.	P.	T.	P.	T.	P.
	mm.		mm.		mm.
25	11·4	65	79·6	105	344·15
30	14·95	70	97·9	110	402·55
35	19·45	75	119·45	115	468·5
40	25·1	80	144·75	120	542·8
45	32·1	85	174·25	125	626·15
50	40·75	90	208·35	130	718·95
55	51·35	95	247·7	135	822·0
60	64·2	100	292·75		

From this, the boiling point at 760 mm. is 132°.

II. *Bromobenzene.*

The preliminary determinations with German soda-glass thermometers are as follows :—

T.	P.	T.	P.	T.	P.
	mm.		mm.		mm.
42·3	11·2	80·8	66·0	116·7	248·3
49·5	16·2	82·8	73·1	122·4	299·1
55·5	21·95	86·8	85·85	123·5	304·7
58·7	25·0	88·8	93·35	125·9	330·6
63·2	31·8	93·4	110·45	129·1	364·7
64·8	33·15	97·45	128·0	134·3	423·8
66·3	36·2	98·6	133·3	138·0	471·1
67·5	38·0	102·8	155·05	143·4	551·4
71·8	44·0	107·3	182·3	147·7	623·3
75·5	54·4	109·3	194·1	150·3	663·2
76·7	56·6	111·6	209·65	154·4	739·3

A comparison was made of the temperatures registered by the lead-glass thermometer and the air thermometer, at the boiling points of aniline and of methyl salicylate. The results of the air thermometer readings will be given under their proper headings. But it must be mentioned here that the readings of the mercury thermometer were

thus compared, for in stating results for bromobenzene, a curve was employed showing the corrections to be applied to the readings of the mercury thermometer to reduce them to readings of the air thermometer. The temperatures given are those read on the mercurial thermometer reduced by means of this curve to readings of the air thermometer.

Series I.				Series II.			
T.	P.	T.	P.	T.	P.	T.	P.
	mm.		mm.		mm.		mm.
100° 57	143·0	140° 04	494·2	155° 22	748·0	140° 25	502·2
110° 91	204·35	151° 01	667·05	129° 15	365·7	149° 9	647·7
120° 34	276·95	155° 64	750·7	119° 85	273·4	155° 22	748·0
130° 02	371·95						

The object in taking the first and last readings in series II at atmospheric pressure was to ascertain whether the zero point of the thermometer had altered during the experiment. The result proved that it had not.

These numbers, smoothed by the method of differences, give—

T.	P.	T.	P.	T.	P.
	mm.		mm.		mm.
45	12·4	85	78·6	125	320·8
50	16·0	90	96·0	130	372·65
55	20·5	95	116·4	135	430·75
60	26·1	100	140·1	140	495·8
65	33·0	105	167·4	145	568·35
70	41·4	110	198·7	150	649·05
75	51·6	115	234·4	155	738·55
80	63·9	120	274·9	160	837·45

III. Aniline.

The preliminary determinations with soda-glass thermometers corrected for calibration, alteration of zero point, &c., are as follows:—

T.	P.	T.	P.	T.	P.
	mm		mm.		mm.
77°·4	16·2	141°·9	219·4	166°·65	474·3
85·8	24·1	144·45	237·8	168·65	497·1
93·0	33·6	147·2	260·6	169·2	507·4
99·0	43·8	147·55	263·6	171·6	542·4
105·1	56·5	150·15	286·0	171·8	544·1
110·4	70·6	152·45	307·1	173·7	575·6
118·0	94·6	152·5	307·0	174·95	592·7
123·3	114·8	155·05	333·3	176·1	612·1
124·5	118·8	157·2	355·5	177·8	638·8
128·45	137·1	157·2	356·3	178·1	646·2
129·95	145·25	159·95	387·6	180·55	690·7
132·15	156·2	161·55	406·6	181·15	701·5
134·6	169·9	162·15	411·9	182·1	719·8
135·65	177·3	164·0	436·4	184·3	762·2
137·75	191·2	165·4	452·9	184·45	763·6
139·0	199·4				

The results of the air thermometer at the boiling point under atmospheric pressure were as follows:—

T. (Hg).	B.	P.	V.	P. V.	Mean P. V.	Hg ₁₈₄ .	T. (air).
		mm					°
184° 52	750·0	1242·2	15 228	18,916	—	12·6	—
rising to	to	1228·45	15 395	18,913	—	„	—
184·72	750·1	1220·2	15·497	18,909	—	„	—
owing to		1211·25	15·613	18,911	—	„	—
alteration		1198·85	15 778	18,915	—	„	—
of bulb		1186·55	15·941	18,915	—	„	—
during		1174·70	16·099	18,912	—	„	—
experiment.		1166·85	16·220	18,926	18,914	„	184·01

A few determinations were then taken with the English thermometer and corrected so as to register temperatures of an air thermometer.

T.	P.	T.	P.	T.	P.
	mm.		mm.		mm.
135°·22	175·4	150°·06	284·6	172°·06	547·5
141·79	216·0	161·12	399·1	183·87	748·5

The curve was slightly altered to coincide with these results; and by the method of differences the following numbers were cal-

T.	P.	T.	P.	T.	P.
	mm.		mm.		mm.
80	18·8	120	100·4	160	386·0
85	24·0	125	120·8	165	447·1
90	30·1	130	144·7	170	515·6
95	37·3	135	172·5	175	592·05
100	45·9	140	204·6	180	677·15
105	56·2	145	241·5	185	771·5
110	68·5	150	283·7	190	875·7
115	83·1	155	331·7		

IV. *Methyl Salicylate.*

The preliminary measurements are as follows:—

T.	P.	T.	P.	T.	P.
	mm.		mm.		mm.
68·7	2·25	138·4	63·3	191·3	335·5
72·4	2·75	142·6	73·9	195·8	386·7
89·0	6·7	146·9	85·3	200·3	434·9
94·8	9·6	152·1	103·7	204·3	484·1
97·1	10·7	158·3	126·0	207·3	521·1
98·3	11·6	165·6	158·5	210·7	571·2
100·1	12·6	171·5	189·8	213·6	614·4
113·5	22·6	176·0	219·3	216·3	656·9
114·9	23·8	182·7	266·1	218·8	698·0
125·6	38·0	183·1	269·1	220·9	728·2
125·9	38·3	187·3	298·0	222·4	761·1
134·9	54·8				

The determination of the boiling point under atmospheric pressure with the air thermometer gave the following numbers:—

T. (Hg).	B.	P.	V.	P. V.	Mean P. V.	Hg _{222·7} .	T. (air).
		mm.					°
223·8	748·75	1333·35	15·386	20,517	—	37·5	—
constant.	to	1306·50	15·696	20,507	—	—	—
	748·95	1295·05	15·829	20,498	—	—	—
		1285·2	15·974	20,530	—	—	—
		1275·7	16·211	20,528	—	—	—
		1261·0	16·525	20,514	20,515	—	222·7

The following measurements were made with the English thermometer, its readings being reduced to those of an air thermometer:—

T.	P.	T.	P.	T.	P.
	mm.		mm.		mm.
222°·4	748·0	190°·0	329·8	219°·9	706·8
169·85	183·8	199·65	426·8	222·4	748·0
179·7	246·4	210·7	566·2	—	—

To ensure coincidence with these readings, the curve required more alteration than in the previous cases. At 222° the alteration amounted to 0·35° rise, whilst at 170° the maximum decrease was 0·5°.

By the method of differences, the following series were calculated:—

T.	P.	T.	P.	T.	P.
	mm.		mm.		mm.
70	2·4	125	37·1	180	249·35
75	3·4	130	45·3	185	287·8
80	4·6	135	55·05	190	330·85
85	6·05	140	66·55	195	378·9
90	7·8	145	80·0	200	432·35
95	9·95	150	95·6	205	491·7
100	12·6	155	113·6	210	557·5
105	15·85	160	134·25	215	630·15
110	19·8	165	157·85	220	710·1
115	24·55	170	184·7	225	798·05
120	30·25	175	215·1		

V. Bromonaphthalene.

The preliminary determinations gave the following numbers:—

Series I.

T.	P.	T.	P.	T.	P.
	mm.		mm.		mm.
113°·6	4·0	196°·8	91·8	251°·3	417·8
121·1	5·8	201·4	106·4	251·7	417·9
129·9	9·0	206·9	125·8	252·0	419·3
140·0	13·2	214·2	155·5	254·4	443·0
149·5	19·3	219·3	177·9	254·6	444·0
158·4	26·7	225·0	209·0	258·7	488·1
167·6	37·7	228·6	223·4	262·5	528·3
174·5	45·0	232·7	256·6	265·8	569·9
175·2	48·0	236·7	288·1	269·8	620·2
183·2	62·4	241·0	317·5	273·1	663·0
186·5	71·3	245·8	358·7	276·7	718·2
187·3	69·2	247·7	380·2	279·8	761·2
193·2	85·5	248·9	390·2		

Boiling point at 761.2 mm., with stem entirely in vapour, 279.9°.

A second series of experiments was carried out with three thermometers, all of German manufacture, which were, as usual, calibrated, and their fixed points determined.

Series II.

P.	T ₁ .	T ₂ .	T ₃ .	Mean.
mm.				
115.7	202.8	203.7	202.85	203.1
136.6	208.6	209.95	209.4	209.3
159.4	214.2	214.9	214.2	214.4
176.6	217.75	218.35	218.0	218.0
195.9	221.75	222.2	221.85	221.9
217.8	225.7	226.0	225.65	225.8
238.3	229.1	229.55	229.0	229.25
264.3	—	233.55	233.1	233.3
292.7	—	237.7	237.1	237.4
340.2	—	244.55	244.4	244.5
400.5	—	250.25	250.1	250.2
454.8	—	255.45	255.5	255.5
512.0	—	260.65	260.5	260.6
600.3	—	268.15	268.15	268.18
671.7	—	273.2	273.3	273.25
747.6	—	278.05	278.2	278.1

These observations, although fairly coincident with the ones already given, yet fall below the latter nearly 1°, from 205° to 225°; the difference diminishes up to 244°, where it is zero; and this remains constant up to 268°. Series II, again, falls slightly below series I up to the boiling point under atmospheric pressure, when the difference amounts to 0.8°.

As it was doubted whether so large a piece of apparatus as the air thermometer would give correct readings at so high a temperature as 280°, on account of unequal heating, and as the correction for the vapour-pressure of mercury was so large, a thermometer was constructed, the principle of which depended on the measurement of the vapour-pressure of mercury. It is necessary to rely on Regnault's results for temperature; and as Regnault determined the temperatures at which mercury boils by means of an air thermometer, the process really is an indirect method of comparing temperatures with those of Regnault's air thermometer. The very great care which Regnault took in these experiments justifies this course. The vapour-pressures of mercury only become sufficiently high to admit of accurate measurement at about 250°. Hence the number of determinations was limited.

The general arrangement of the apparatus was similar to that

employed in the air thermometer determinations. The bulb A was dispensed with, and the exit tube sealed at F. This U tube was then filled with mercury, and repeatedly boiled out so as to secure absence of air. On applying heat to the U tube, and reducing the pressure by means of the pump B, vapour was evolved from the mercury in the closed limb, and the pressure which it exerted was calculated by readings of the different heights of the mercury in the limbs of the U tube, and on a gauge at E, similar to that at C, by which the differential gauge was replaced. It is seen that no calibration is required; and indeed the process is a simple and, we believe, accurate means for the measurement of high temperatures.

The following results were obtained:—

Pressure of bromo-naphthalene.	Pressure of mercury vapour.	Temperature from Regnault's data.
756.2 mm.	157.15 mm.	280.6°
612.8	124.35	270.35

These results were checked several times.

We now possessed the means of correcting the English thermometer, so as to reduce it to air-readings. The correction to be applied at 280° amounted to - 2.43. The correction to be applied for intermediate temperatures was found from this determination, and from the previous determinations with the air thermometer by the graphic method.

A number of readings of the vapour-pressure of bromonaphthalene were finally made with the English thermometer. They are as follows, and the temperatures given are reduced to those of an air thermometer. As the zero point of the thermometer rose 0.5 during these experiments, this change may be assumed either to have occurred gradually, or to have taken place immediately after the liquid was heated. If the latter view is taken, the results make the vapour-pressures of alcohol concordant when methyl salicylate and when bromonaphthalene were used as jackets. We have, therefore, supposed that the change took place at once.

T.	P.	T.	P.	T.	P.
	mm.		mm.		mm
280.22	751.3	219.36	178.2	259.53	480.4
204.54	118.0	231.14	241.5	270.02	608.3
204.84	119.1	240.98	310.8	280.3	752.5
209.78	137.55	250.83	392.6		

The mean results, as in former cases, were obtained by the method

T.	P.	T.	P.	T.	P.
	mm.		mm.		mm.
110	3·6	170	40·75	230	235·95
115	4·4	175	48·05	235	267·85
120	5·45	180	56·45	240	303·35
125	6·8	185	66·1	245	342·75
130	8·5	190	77·15	250	386·35
135	10·6	195	89·75	255	434·45
140	13·15	200	104·05	260	487·35
145	16·2	205	120·2	265	545·35
150	19·8	210	138·4	270	609·75
155	24·0	215	158·85	275	677·85
160	28·85	220	181·75	280	752·95
165	34·4	225	207·35	285	834·35

The following tables give the vapour-pressures of the substances studied, including those determined by Regnault, for each degree between 0° and 360°, so that any desired temperature may be obtained. For the decimal parts of a degree, simple proportion gives a sufficiently accurate result:—

Carbon Bisulphide.

T.	P.	T.	P.	T.	P.
	mm.		mm.		mm.
0	127·9	17	264·65	34	501·65
1	133·85	18	275·4	35	519·65
2	140·05	19	286·55	36	538·15
3	146·45	20	298·05	37	557·15
4	153·1	21	309·9	38	576·75
5	160·0	22	322·1	39	596·85
6	167·15	23	334·7	40	617·5
7	174·6	24	347·7	41	638·7
8	182·25	25	361·1	42	660·5
9	190·2	26	374·95	43	682·9
10	198·45	27	389·2	44	705·9
11	207·0	28	403·9	45	729·5
12	215·8	29	419·0	46	753·75
13	224·95	30	434·6	47	778·6
14	234·4	31	450·65	48	804·1
15	244·15	32	467·15	49	830·25
16	254·25	33	484·15	50	857·1

Ethyl Alcohol.

T.	P.	T.	P.	T.	P.
	mm.		mm.		mm.
40	133·7	54	265·9	68	497·25
41	140·75	55	278·6	69	518·85
42	148·1	56	291·85	70	541·2
43	155·8	57	305·65	71	564·35
44	163·8	58	319·95	72	588·35
45	172·2	59	334·85	73	613·2
46	181·0	60	350·3	74	638·95
47	190·1	61	366·4	75	665·55
48	199·65	62	383·1	76	693·1
49	209·6	63	400·4	77	721·55
50	220·0	64	418·35	78	751·0
51	230·8	65	437·0	79	781·45
52	242·05	66	456·35	80	812·9
53	253·8	67	476·45		

Chlorobenzene.

T.	P.	T.	P.	T.	P.
	mm.		mm.		mm.
70	97·9	91	215·8	112	427·95
71	101·95	92	223·45	113	441·15
72	106·1	93	231·3	114	454·65
73	110·41	94	239·35	115	468·5
74	114·85	95	247·7	116	482·65
75	119·45	96	256·2	117	497·2
76	124·2	97	265·0	118	512·05
77	129·1	98	274·0	119	527·25
78	134·15	99	283·25	120	542·8
79	139·4	100	292·75	121	558·7
80	144·8	101	302·5	122	575·05
81	150·3	102	312·5	123	591·7
82	156·05	103	322·8	124	608·75
83	161·95	104	333·35	125	626·15
84	168·0	105	344·15	126	643·95
85	174·25	106	355·25	127	662·15
86	181·7	107	366·65	128	680·75
87	187·3	108	378·3	129	699·65
88	194·1	109	390·25	130	718·95
89	201·15	110	402·55	131	738·65
90	208·35	111	415·1	132	758·8

Bromobenzene.

T.	P.	T.	P.	T.	P.
	mm.		mm.		mm.
120	274·9	134	418·6	148	615·75
121	283·65	135	430·75	149	632·25
122	292·6	136	443·2	150	649·05
123	301·75	137	455·9	151	666·25
124	311·15	138	468·9	152	683·8
125	320·8	139	482·2	153	701·65
126	330·7	140	495·8	154	719·95
127	340·8	141	509·7	155	738·55
128	351·15	142	523·9	156	757·55
129	361·8	143	538·4	157	776·95
130	372·65	144	553·2	158	796·7
131	383·75	145	568·35	159	816·9
132	395·1	146	583·85	160	837·45
133	406·7	147	599·65		

Aniline.

T.	P.	T.	P.	T.	P.
	mm.		mm.		mm.
150	283·7	162	409·6	174	576·1
151	292·8	163	421·8	175	592·05
152	302·15	164	434·3	176	608·35
153	311·75	165	447·1	177	625·05
154	321·6	166	460·2	178	642·05
155	331·7	167	473·6	179	659·45
156	342·05	168	487·25	180	677·15
157	352·65	169	501·25	181	695·3
158	363·5	170	515·6	182	713·75
159	374·6	171	530·2	183	732·65
160	386·0	172	545·2	184	751·9
161	397·65	173	560·45	185	771·5

Methyl Salicylate.

T.	P.	T.	P.	T.	P.
	mm.		mm.		mm.
175	215·1	184	279·75	193	339·05
176	221·65	185	287·8	194	368·85
177	228·3	186	296·0	195	378·9
178	235·15	187	304·45	196	389·15
179	242·15	188	313·05	197	399·6
180	249·35	189	321·85	198	410·3
181	256·7	190	330·85	199	421·2
182	264·2	191	340·05	200	432·35
183	271·9	192	349·45	201	443·75

Methyl Salicylate—continued.

T.	P.	T.	P.	T.	P.
	mm.		mm.		mm.
202	455·35	210	557·5	218	677·25
203	467·25	211	571·45	219	693·6
204	479·35	212	585·7	220	710·1
205	491·7	213	600·25	221	727·05
206	504·35	214	615·05	222	744·35
207	517·25	215	630·15	223	761·9
208	530·4	216	645·55	224	779·85
209	543·8	217	661·25	225	798·1

Bromonaphthalene.

T.	P.	T.	P.	T.	P.
	mm.		mm.		mm.
215	158·85	238	288·7	260	487·35
216	163·25	239	295·95	261	498·55
217	167·7	240	303·35	262	509·9
218	172·3	241	310·9	263	521·5
219	176·95	242	318·65	264	533·35
220	181·75	243	326·5	265	545·35
221	186·65	244	334·55	266	557·6
222	191·65	245	342·75	267	570·05
223	196·75	246	351·1	268	582·7
224	202·0	247	359·65	269	595·6
225	207·35	248	368·4	270	608·75
226	212·8	249	377·3	271	622·1
227	218·4	250	386·35	272	635·7
228	224·15	251	395·6	273	649·5
229	230·0	252	405·05	274	663·55
230	235·95	253	414·65	275	677·85
231	242·05	254	424·45	276	692·4
232	248·3	255	434·45	277	707·15
233	254·65	256	444·65	278	722·15
234	261·2	257	455·0	279	737·45
235	267·85	258	465·6	280	752·95
236	274·65	259	476·35	281	768·7
237	281·6				

Mercury.

T.	P.	T.	P.	T.	P.
	mm.		mm.		mm.
270	123·0	274	135·05	278	148·15
271	125·9	275	138·2	279	151·6
272	128·85	276	141·45	280	155·15
273	131·9	277	144·75	281	158·7

Mercury—continued.

T.	P.	T.	P.	T.	P.
	mm.		mm.		mm.
282	162·35	309	293·55	335	497·7
283	166·1	310	299·7	336	507·5
284	169·9	311	306·1	337	517·55
285	173·8	312	312·55	338	527·65
286	177·75	313	319·2	339	537·95
287	181·8	314	325·85	340	458·35
288	185·95	315	332·7	341	559·2
289	190·15	316	339·65	342	569·95
290	194·45	317	346·8	343	580·95
291	198·75	318	353·95	344	592·2
292	203·2	319	361·3	345	603·6
293	207·75	320	368·75	346	615·25
294	212·4	321	376·4	347	626·95
295	217·1	322	384·1	348	638·9
296	221·95	323	391·95	349	651·1
297	226·8	324	400·0	350	663·2
298	231·8	325	408·1	351	675·85
299	236·9	326	416·45	352	688·55
300	242·15	327	424·85	353	701·55
301	247·5	328	433·45	354	714·75
302	252·85	329	442·15	355	728·05
303	258·4	330	450·9	356	741·55
304	263·95	331	460·1	357	755·35
305	269·6	332	469·2	358	769·4
306	275·45	333	478·55	359	783·5
307	281·35	334	488·05	360	797·75
308	287·4				

The authors beg, in conclusion, to request those chemists and physicists who make use of these tables kindly to inform them of any discrepancy which they may observe, or to point out any clerical error which they may notice.

LXIX.—*Researches on Secondary and Tertiary Azo-Compounds.*
No. III.

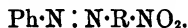
By RAPHAEL MELDOLA, Professor of Chemistry in the Finsbury Technical College, City and Guilds of London Institute.

It has been shown in former communications (*Chem. Soc. Trans.*, 1883, 425, and 1884, 106) that a nitro-group occupying a para-position with respect to an azo-group can be reduced by ammonium sulphide without severing the azo-nitrogen atoms. The amido-

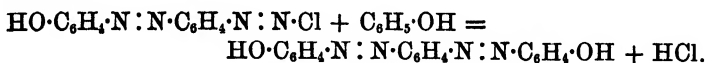
azo-compounds thus produced can then be again diazotised and combined with phenols or amines so as to form secondary and tertiary azo-compounds, of which substances numerous types were prepared and described.

Since the publication of the papers referred to a method of producing similar compounds has been published by Nietzki (*Ber.*, **17**, 343), which method I had also employed in the early part of these researches for the preparation of the compounds $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ and $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH}$, but as the results have not been published, priority must be given to Nietzki. The method in question consisted in reducing paranitracetanilide with iron and acetic acid (I employed zinc-dust and acetic acid), diazotising the paramidoacetanilide, and combining with phenols or amines, the acetyl-group being afterwards removed by hydrolysis. Among other recent contributions to the present subject I may mention that it has been shown by Griess (*Ber.*, **17**, 607) that under certain conditions both amido-groups in paradiamines can be directly diazotised, and secondary azo-compounds prepared by this method.

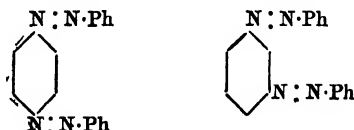
The object of the present paper is to show the extension of the principle of the reduction of a nitro-azo-compound by ammonium sulphide to phenolic nitro-azo-derivatives of the general formula—



Such a compound on reduction and diazotising would furnish, when combined with phenols, secondary azo-compounds, in accordance with the equation—



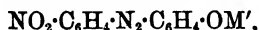
These secondary azo-compounds are related to those obtained by Wallach from metadiamines (*Ber.*, **15**, 2825 and 3020) in the following manner :—



I. ACTION OF DIAZOPARANITROBENZENE UPON PHENOL.

Paranitrobenzene-azophenol, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$.—Paranitraniline was diazotised in the usual way, and mixed with an alkaline solution containing the theoretical quantity of phenol dissolved in sodium hydroxide. A bulky brown gelatinous precipitate separated out, and

this after being collected and washed, became ochreous on acidification with dilute hydrochloric acid. After crystallisation from dilute alcohol the substance was finally obtained in the form of large golden scale-like crystals, having a melting point of 183—184°, and readily soluble in alcohol, acetone, acetic acid and benzene, the solutions being yellow or orange according to their degree of concentration. It is nearly insoluble in water, but dissolves in boiling dilute alkalis with an intense red-brown colour, the corresponding salts,



crystallising out on cooling in lustrous scales. The substance dissolves in strong sulphuric acid with an orange colour.

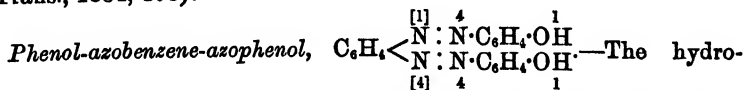
Paramidobenzene-azophenol, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$.—The nitro-azophenol above described was mixed with a small quantity of water and heated with ammonia and ammonium sulphide for about half-an-hour. The deep red-brown solution had by this time changed to yellow, and a glistening ochreous crystalline deposit had formed. The latter was collected, washed, and crystallised from boiling water, in which it dissolves with the formation of a deep yellow solution. The pure substance forms small brown scales melting at 181°. It has distinctly basic properties, dissolving in hot dilute hydrochloric acid, with a magenta-like red colour. On adding platinum chloride solution to a solution of the hydrochloride, the platinumchloride separates out in black scaly crystals.

I. 0.3190 gram gave 0.0747 gram Pt.

II. 0.2084 ,, 0.0489 ,,

	Found	
	I.	II.
Theory for $2(\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}, \text{HCl}), \text{PtCl}_4$.		
Pt.	23.54 per cent.	23.41 23.46

The base is readily soluble in alcohol; the solution is yellow, becoming orange on adding caustic potash. It dissolves in strong sulphuric acid with a yellow colour, which becomes redder on dilution. The amido-group in this compound can be readily diazotised, the diazo-salts decomposing on the addition of ammonia, with the production of the intense blue unstable colouring matter already described as a characteristic reaction of other para-tetrazo-compounds (*Trans.*, 1884, 108).



chloric acid solution of paramidobenzene-azophenol was mixed with a solution of sodium nitrite containing the theoretical quantity of this

salt, and the diazo-chloride then gradually mixed with the necessary quantity of phenol dissolved in dilute alkali. A deep-red solution is formed, but nothing separates until the addition of acid, when a brown gelatinous precipitate forms. The latter on being collected, washed and dried, formed an amorphous brown powder, which could not be crystallised; it is readily soluble in ammonia and the fixed alkalis, with a beautiful red colour. The calcium salt also dissolves with a red colour, but could not be crystallised. The solution of the substance in ammonia dyes wool and silk of a fine golden-yellow colour. The substance is practically insoluble in boiling toluene, chloroform, or alcohol; it dissolves with an orange colour in hot phenol and aniline. With strong sulphuric acid it gives a violet colour, which remains unchanged even on diluting with a considerable quantity of water. The melting point is about 205—207°, but it commences to soften at a much lower temperature.

II. ACTION OF DIAZOPARANITROBENZENE UPON RESORCINOL.

Paranitrobenzene-azoresorcinol, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{OH}$. —

A solution of diazoparanitrobenzene chloride was gradually mixed with the theoretical quantity of resorcinol dissolved in dilute caustic soda. A violet colour was immediately developed on mixing the solutions, and the nitrazo-compound partially separated, but was not completely thrown down until the solution was acidified. A reddish-brown precipitate was thus obtained, which was collected, washed, and dried. The substance then had the appearance of a brick-red powder, which could not be crystallised; it has acid properties, dissolving in caustic alkalis with the production of a violet solution, which becomes bluer on boiling. It forms a soluble calcium salt, which separates in a gelatinous state from the aqueous solution on cooling. The substance is but slightly soluble in boiling alcohol, acetic acid, or toluene; the solutions are of an orange colour, and the compound dissolves in strong sulphuric acid with a similar colour.

Paramidobenzene-azoresorcinol, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{OH}$. —

The foregoing nitrazo-compound is dissolved in a small quantity of dilute caustic soda, and the solution warmed with ammonium sulphide. The contents of the flask must be cooled as soon as the reduction is complete, otherwise the reaction goes too far; the reduction of the NO_2 -group is indicated by the change in colour of the solution from violet to orange, and when this point is reached the solution is just neutralised with hydrochloric acid, and the brown precipitate thus formed is collected, washed, and purified by dissolving in boiling dilute hydrochloric acid, filtering, and reprecipitating by ammonia. The

compound is thus obtained as a brown crystalline substance, soluble with difficulty in hot alcohol, the solution being deep reddish-brown. It has well-marked acid and basic properties, dissolving in dilute acids with a pale orange colour, and in alkalis with a deep reddish-orange. The sulphate separates from a hot solution on cooling, in the form of silvery scales, having the formula—

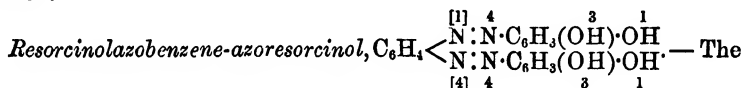


The platinum salt, formed by adding platinum chloride solution to a solution of the hydrochloride of the base, was obtained as a brown non-crystalline powder:—

0.2538 gram gave 0.0570 gram Pt.

Theory for $2(\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}_2\cdot\text{HCl}), \text{PtCl}_4.$	Found.
Pt. 22.67 per cent.	22.46

The melting point of the substance was too high to be determined.



compound last described was diazotised in the usual way, and the solution mixed with an alkaline solution of resorcinol. The tetrazo-chloride solution is of a deep yellowish-orange, and a few drops poured into water and then made alkaline with ammonia, give rise to the production of an intense violet colouring matter, which slowly decomposes on standing. On mixing the solutions of the tetrazo-chloride and resorcinol, a deep violet solution is produced, and on acidifying a brown gelatinous precipitate separates, which, after being collected and washed, dries down to a dull bronzy uncrystallisable powder. The substance is distinctly acid in character, dissolving readily in alkalis with a violet colour; it is almost insoluble in alcohol and acetic acid, imparting only a slight red colour to these liquids when boiled with them, and is quite insoluble in chloroform and toluene. It dissolves in strong sulphuric acid with a violet colour.

III. ACTION OF DIAZOPARANITROBENZENE UPON THE NAPHTHOLS.

Paranitrobenzene-azo- α -naphthol, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N} \cdot \text{N} \cdot \text{C}_{10}\text{H}_7\cdot\text{OH}$. — When a solution of paranitrodiazobenzene chloride is mixed with an alkaline solution of α -naphthol, a violet colour is first produced, and a dark precipitate afterwards separates. The latter was collected, washed with water, then with dilute hydrochloric acid, and finally with water, until free from acid. The substance was obtained on drying

in the form of a dull red uncrystallisable powder, having too high a melting point to be determined by a mercury thermometer. It dissolves in hot aqueous soda with a fine blue colour, and with a similar colour in alcoholic ammonia. It is almost insoluble in boiling alcohol, and but slightly soluble in acetic acid, toluene, and chloroform. It dissolves in strong sulphuric acid with a violet colour.

Paramidobenzene-azo- α -naphthol, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{N} \cdot \text{C}_{10}\text{H}_7 \cdot \text{OH}$. — The preceding nitrazo-compound was dissolved in hot dilute caustic soda and reduced by ammonium sulphide; the colour of the solution changes from blue to red, and the amido-compound is precipitated on adding hydrochloric acid as a brown gelatinous precipitate drying to a dark-brown uncrystallisable powder. The freshly precipitated substance is slightly soluble in boiling water; the dry solid is readily dissolved by hot alcohol, and with some difficulty by toluene and glacial acetic acid. The solutions are ochreous or dull orange. The substance is somewhat acid in character, dissolving in aqueous alkalis with a red colour, and being precipitated by acids; the presence of the NH_2 -group also confers a feebly basic character upon the compound, which is shown by its dissolving with a fine violet-red colour in alcohol acidified with hydrochloric acid. It dissolves in strong sulphuric acid with a red colour passing into orange on dilution.

Paranitrobenzene-azo- β -naphthol, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{N} \cdot \text{C}_{10}\text{H}_7 \cdot \text{OH}^*$. — On mixing solutions of paranitrodiazobenzene chloride and sodium β -naphtholate, a bulky bright reddish-orange precipitate at once forms. This substance, after being collected, washed, and dried, showed the following properties: it was almost insoluble in boiling alcohol, but soluble in alcoholic soda with a violet colour. It was moderately soluble in hot glacial acetic acid, the solution being orange and the substance separating on cooling in beautiful orange needles. It dissolved also in hot toluene with an orange colour, the solution on cooling depositing the substance in the form of orange-brown scaly crystals, having a slight metallic reflection and melting sharply at 249° . Unlike the corresponding substance from α -naphthol,

* The formulæ of these β -azo-compounds have been written on the above type provisionally, until further insight is gained into their constitution. For reasons stated in my last communication, I am, however, disposed to accept Liebermann's view, and to regard these bodies as having the constitution—



(*Trans.*, 1884, 118.) The arguments recently advanced by Lawson (*Ber.*, 18, 796) in favour of the view that the azo-derivative of β -naphthylamine are diazo-amido-compounds, appear to me to be perfectly inconclusive. (See also a note by Zincke appended to Lawson's paper, *loc. cit.*, p. 802.) “

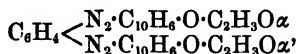
the present compound is quite insoluble in hot aqueous alkalis. It dissolves in strong sulphuric acid with a magenta-like red colour, which changes into orange on dilution.

Paramidobenzene-azo-β-naphthol, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}^1\text{:N}^4\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}^\beta$. — In order to reduce the foregoing compound, it was found most advantageous to get it into a semi-gelatinous state by dissolving it in hot alcoholic soda, and pouring the solution into water acidified with hydrochloric acid. The precipitate was collected, washed thoroughly with water, and then transferred to a flask and warmed with ammonia and ammonium sulphide. In about 15 minutes, the bright orange precipitate had changed to brown, and the amido-compound, after being collected and washed, dried to a dull, bronzy, uncrystallisable substance. It dissolves in hot alcohol with an orange colour, and is also soluble in boiling toluene and glacial acetic acid; it separates from its solutions in a flocculent state. It is slightly soluble in boiling dilute caustic soda with a reddish colour, but is far less soluble than the corresponding α-naphthol compound; it readily dissolves in alcoholic soda with an orange colour. It is insoluble in a mixture of alcohol and hydrochloric acid, so that this substance is less basic than the corresponding α-naphthol compound. The colour reaction with strong sulphuric acid is similar to that observed before reduction, viz., magenta-like red passing into orange on dilution.

α-Naphtholazobenzene-azo-α-naphthol, $\text{C}_6\text{H}_4\cdot\begin{matrix} 1 & \alpha & \\ \text{N}:\text{N} & \cdot & \text{C}_{10}\text{H}_6\cdot\text{OH}^\alpha \\ 4 & \alpha & \\ \text{N}:\text{N} & \cdot & \text{C}_{10}\text{H}_6\cdot\text{OH}^\alpha \end{matrix}$. — Par-

amidobenzene-azo-α-naphthol was diazotised in an alcoholic solution by means of hydrochloric acid and sodium nitrite; the solution of the tetrazo-chloride is orange and gives a fine blue coloration on the addition of ammonia. On mixing the solution with α-naphthol dissolved in dilute caustic soda, a deep indigo-blue colour is developed; but nothing separates until acid is added, when a dark precipitate is thrown down. The latter is collected, washed, redissolved in hot caustic soda, the solution filtered, and reprecipitated by hydrochloric acid. This process of purification was repeated two or three times, and the substance was finally obtained, after drying, in the form of a green powder with a metallic lustre. This secondary azo-compound dissolves but very slightly in acetic acid, alcohol, or toluene; it is more readily soluble in boiling aniline, the solution being red, but the substance is not deposited therefrom in a crystalline form. It readily dissolves in dilute caustic soda with a fine blue colour. Heated in a dry tube, it froths up and decomposes. It dissolves in strong sulphuric acid, giving a clear blue solution, which becomes violet on dilution.

By heating the foregoing compound with acetic anhydride and dry powdered sodium acetate, the acetyl-derivative,



was obtained as an orange uncrystallisable substance, melting at about 223°.



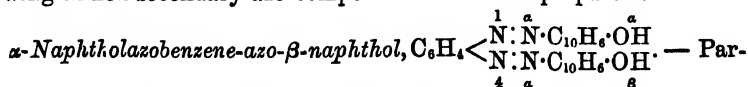
order to diazotise paramidobenzene-azo-β-naphthol, this substance is dissolved in alcoholic soda, acidified with hydrochloric acid, and the necessary quantity of sodium nitrite dissolved in water gradually run into the well-cooled solution. The tetrazo-chloride solution, which is of an orange colour, gives the blue reaction with ammonia in a very striking manner, and on mixing with an alkaline solution of β-naphthol, a secondary azo-compound is at once precipitated as a violet substance, which, after washing and drying, is obtained as a dull bronzy powder. The substance is insoluble in boiling alcohol or aqueous alkaline solutions; it dissolves in alcoholic soda with a violet colour. It is dissolved with difficulty by hot toluene, the solution being magenta-red; boiling aniline dissolves it more readily, the solution being reddish-violet when hot, bluer when cold. The substance was crystallised from hot aniline, and obtained in the form of small metallic green glistening needles, which were freed from aniline by washing with alcohol.

0.2142 gram burnt with copper oxide and oxygen gave 0.5837 gram CO₂ and 0.0888 gram H₂O.

	Theory for C ₂₆ H ₁₈ N ₄ O ₂ .	Found.
C.....	74.64 per cent.	74.32 per cent.
H	4.30 „	4.60 „

The substance dissolves in strong sulphuric acid with a bright blue colour, becoming violet on dilution. The melting point is above 275°. A trace of some bye-product, or possibly of an isomeride, was found in the aniline mother-liquor, but the quantity was too small for further examination.

Starting from the corresponding amidoazo-compounds, the following mixed secondary azo-compounds have been prepared:—



amidobenzene-azo-α-naphthol is diazotised in the usual way, and the solution mixed with an alkaline solution of β-naphthol. A deep

violet precipitate forms; this dries to a dull bronzy powder, very slightly soluble in boiling alcohol, but more soluble in boiling toluene and glacial acetic acid, the solutions being reddish-violet. It separates from the toluene solution, on cooling, as a dull bronzy green non-crystalline powder, melting at 235—236°. It dissolves slightly in boiling dilute aqueous caustic soda and readily in alcoholic soda, with a blue colour. With strong sulphuric acid, it gives the same colour reaction as the previous compound.

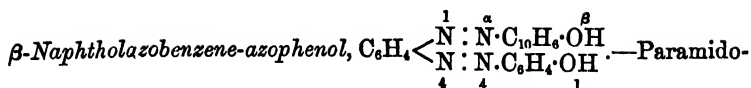
The β -naphthol-disulphonic acid (sodium salt) corresponding to the above compound, $C_6H_4 < \begin{smallmatrix} N_2 \cdot C_{10}H_6 \cdot OH\alpha \\ N_2 \cdot C_{10}H_4(SO_3H)_2 \cdot OH\beta \end{smallmatrix}$, is precipitated in the form of a violet gelatinous sodium salt, when a solution of the requisite tetrazo-chloride is mixed with an alkaline solution of the sodium salt of β -naphthol-disulphonic acid. From an acid bath it dyes wool, &c., of an indigo-blue shade.

The same mode of preparation furnishes the corresponding β -naphthol compound, $C_6H_4 < \begin{smallmatrix} N_2 \cdot C_{10}H_6 \cdot OH\beta \\ N_2 \cdot C_{10}H_4(SO_3H)_2 \cdot OH\beta \end{smallmatrix}$, which is similar in appearance and general properties, but appears to be of great stability and fastness as a dye. The shades produced are of a fine indigo-blue.

α -Naphtholazobenzene-azophenol, $C_6H_4 < \begin{smallmatrix} \overset{1}{N} : \overset{\alpha}{N} \cdot C_{10}H_6 \cdot \overset{\alpha}{OH} \\ \underset{4}{N} : \underset{4}{N} \cdot C_6H_4 \cdot \underset{1}{OH} \end{smallmatrix}$.—This compound is obtained by combining diazotised paramidobenzene-azo- α -naphthol with phenol in an alkaline solution. The yield is small, and the dried product forms a dark uncrystallisable powder soluble in dilute caustic alkalis with a dull red colour. It dissolves slightly in boiling toluene with an orange and in boiling alcohol and acetic acid with a red colour; it is freely soluble in alcoholic soda with a deep claret-red colour. With strong sulphuric acid it gives an indigo-blue colour.

α -Naphtholazobenzene-azoresorcinol, $C_6H_4 < \begin{smallmatrix} \overset{1}{N} : \overset{\alpha}{N} \cdot C_{10}H_6 \cdot \overset{\alpha}{OH} \\ \underset{4}{N} : \underset{4}{N} \cdot C_6H_3(OH)_2 \cdot \underset{1}{OH} \end{smallmatrix}$.—

On mixing the solution of tetrazo-chloride with the necessary quantity of resorcinol dissolved in dilute caustic soda, a deep violet solution is obtained from which acids throw down a brown gelatinous precipitate, drying to a bronzy green uncrystallisable powder, slightly soluble in toluene, acetic acid, and acetone, less soluble in chloroform: these solutions are all red. The freshly precipitated substance dissolves in hot alcohol with a red colour. The dry substance dissolves in hot aniline with a red colour and in aqueous alkalis, including ammonia, with a violet; in presence of excess of caustic alkali the solution is blue. Heated in a dry tube the substance swells up and decomposes without previous fusion.

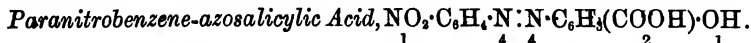


benzene-azo- β -naphthol was diazotised in the manner before described and the tetrazo-chloride mixed with an alkaline solution of phenol. A violet solution is first produced, and on acidifying a brown precipitate is formed; the latter on being collected on a filter and washed, dries down to a reddish powder dissolving in boiling alcohol and toluene with a red colour: the alcoholic solution becomes bluish-violet on adding ammonia. The substance separates from its alcoholic solution in microscopic filamentous crystals, and from the toluene solution in the form of warty concretions of a bronzy green colour, melting at about 225° , but softening before this temperature is reached. It dissolves in aqueous alkalis with a reddish-violet colour, and in strong sulphuric acid with a bluish-green becoming violet on dilution.

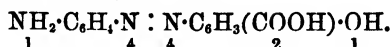


On mixing the necessary solutions and acidulating a gelatinous brown precipitate forms which dries to a bronzy green powder soluble with a red colour in boiling alcohol and less readily in toluene with a similar colour. It has a distinctly acid character, dissolving readily in dilute aqueous alkalis with a violet colour. With strong sulphuric acid it gives a deep bluish-green colour.

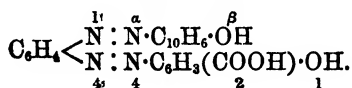
IV. ACTION OF DIAZOPARANITROBENZENE UPON SALICYLIC ACID.



—A solution of diazotised paranitraniline was mixed with a well-cooled solution containing the necessary quantity of salicylic acid dissolved in excess of caustic soda. A reddish colour was at once developed, and on acidifying the solution an ochreous precipitate separated. The latter was collected, washed, dissolved in hot dilute ammonia, filtered, and again precipitated by acid. The substance was finally obtained in the form of glistening orange-brown needles by crystallisation from dilute acetic acid. It is a distinctly acid substance, dissolving in dilute alkalis, including ammonia, with a deep reddish-orange colour; it dissolves readily in alcohol and acetic acid, and less readily in boiling toluene, the solutions being of an orange colour. Sulphuric acid dissolves it with a similar colour. The melting point could not be determined with precision, as at 225° the substance commences to blacken.

Paramidobenzene-azosalicyclic Acid,

—The sodium salt of the preceding compound was obtained by dissolving the substance in dilute caustic soda and then saturating the solution with common salt; a brown pulpy precipitate was thrown down, and was collected and reduced by warming it with ammonia and ammonium sulphide. The substance soon dissolved, forming a deep yellow solution of the amido-compound which was precipitated by hydrochloric acid as a flesh-coloured flocculent precipitate. The latter was purified by dissolving in ammonia, filtering, and reprecipitating by acid. The amido-compound is still acid, dissolving in ammonia and the caustic alkalis with a yellow colour. It dissolves slightly in boiling water, and on acidifying a hot solution of the sodium or ammonium salt, the acid separates out on cooling in the form of small colourless needles, melting and at the same time blackening at 219–220°. It is insoluble in toluene, but dissolves readily in hot alcohol with an orange, and slightly in acetic acid with a magenta-red colour. The alcoholic solution becomes red on the addition of hydrochloric acid.

β-Naphtholazobenzene-azosalicyclic Acid,

—Paramidobenzene-azosalicyclic acid was dissolved in dilute alcohol acidified with hydrochloric acid and the necessary quantity of sodium nitrite dissolved in water added to the well-cooled solution. The solution of the tetrazo-chloride was of an orange colour and gave an intense blue coloration on the addition of ammonia: on mixing with an alkaline solution of β-naphthol a reddish-brown gelatinous secondary azo-compound was at once precipitated. The latter, after being collected and washed, dried down to a brown substance, which was crystallised from boiling aniline, the crystals, which consisted of microscopic brown needles, being washed first with benzene, then with alcohol, and finally with dilute hydrochloric acid and water.

0.2213 gram burnt with copper oxide and oxygen gave 0.5408 gram CO₂ and 0.0801 gram H₂O.

Theory for C ₂₃ H ₁₆ N ₄ O ₄ .		Found.
C.	66.99 per cent.	66.64 per cent.
H.	3.88 „	4.02 „

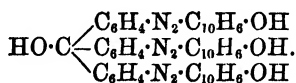
The substance is almost insoluble in boiling toluene, imparting only a slight red colour to the solution; it dissolves slightly in glacial

acetic acid, chloroform, and alcohol, the solutions being in all cases of a magenta-like red. It dissolves in aqueous caustic alkalis with a reddish-violet colour, and is precipitated by acids in a gelatinous state. With strong sulphuric acid it gives a greenish-blue passing into violet on dilution. The melting point was too high to be determined, but is above 255° .

Paramidobenzene-azosalicyclic acid when diazotised could not be made to combine with another molecule of salicylic acid, nor with the sulphonic acids of the naphthols.

In order to ascertain whether the corresponding azo-derivatives of metanitriline could be obtained, metanitrobenzene-azo- β -naphthol was prepared by mixing a solution of metanitrodiazobenzene chloride with an alkaline solution of β -naphthol. An orange precipitate immediately forms, and after being washed and dried the substance was obtained pure by crystallisation from toluene in the form of orange scales having a bright metallic lustre. The formula of this nitrazo-compound may be written:— $\text{NO}_2\cdot\underset{1}{\text{C}_6\text{H}_4}\cdot\underset{3}{\text{N}}:\underset{a}{\text{N}}\cdot\underset{\beta}{\text{C}_{10}\text{H}_6}\cdot\text{OH}$. It is insoluble in aqueous caustic alkalis, but dissolves in alcoholic potash with a reddish-orange colour. Its melting point is $191\text{--}192^{\circ}$, and it gives with strong sulphuric acid a magenta-like red coloration passing into orange on dilution. It could not be reduced by means of ammonium sulphide, and was thus incapable of serving as a source of secondary azo-compounds.

In concluding this section of the present researches upon the azo-compounds, I may call attention to the existence of a new class of tertiary azo-compounds derived from the rosanilines by diazotising and combining with phenols in alkaline solutions. Of these compounds the naphthol-derivatives have been prepared and have been obtained in the form of orange uncrystallisable powders of which the formula is probably—



Both para and ordinary rosaniline furnish these derivatives, which appear to be very stable. They dye silk and wool of an orange colour but are not likely to be of much technical value. The colouring matters produced by the action of diazotised rosaniline upon the sulphonic acids of the naphthols are very unstable.

LXX.—*Note on the Spontaneous Polymerisation of Volatile Hydrocarbons at the ordinary Atmospheric Temperature.*

By Sir HENRY E. ROSCOE, F.R.S.

SOME time ago a small quantity of a white crystalline camphor-like substance was sent to me by Mr. W. W. Staveley of West Bromwich, with the information that it had been obtained by him from the most volatile portions of the hydrocarbons, resulting from the decomposition of crude phenol at a red heat. Mr. Staveley writes, "after standing for some weeks the greater portion of the volatile bodies, boiling from 20° to 40° , was changed by absorption of atmospheric oxygen into bodies boiling between 160° and 170° . After distilling off the lighter portion from the oxidised mixture, the residue in the retort, on cooling, solidified to a white crystalline mass."

Examination of this product has proved that the above supposition is incorrect, and that the crystalline body is a hydrocarbon having the formula $C_{10}H_{12}$. For the purpose of purification the crude material, which had a yellow colour and was saturated with liquid, was pressed between filter-paper and afterwards distilled in a vacuum, when it came over without decomposition at about 63° under 9 mm. pressure, but is found to decompose when distilled under the ordinary pressure. The hydrocarbon thus purified is perfectly colourless, crystallising in brilliant stellar clusters which melt at 32.9° . It volatilises slowly at the ordinary temperature like camphor, crystals being deposited on the upper part of the vessel containing it. Analysis gave:—

	1.	2.	3.	Mean.
Carbon	90.78	90.79	90.96	90.84
Hydrogen	9.59	8.69	9.27	9.18
	<hr/> 100.37	<hr/> 99.48	<hr/> 100.23	<hr/> 100.02

The vapour-density by Hofmann's method gave:—

	1.	2.
Weight of substance	0.0728 gram.	0.1777 gram.
Barometer reduced.....	760.7 mm.	760.7 mm.
Mercurial column	686.2 mm.	587.0 mm.
Volume of vapour	170.1 c.c.	206.3 c.c.
Temperature of vapour....	100°	132°
Vapour-density	4.39	4.57
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The molecular formula $C_{10}H_{12}$ requires a v. d. of 4.57, and the percentage composition $C = 90.9$, $H = 9.10$.

The sp. gr. of the solid hydrocarbon is 1.012 at $17^{\circ}5$, the crystals sinking under water in a vacuum. It dissolves readily in petroleum spirit, ether, and alcohol, and has a peculiar smell, resembling but distinct from that of camphor. On exposure to air it rapidly absorbs oxygen, and is converted into a yellow resin.

When heated in a vacuum tube at 180° for four hours the compound undergoes further polymerisation, and an opaque white buttery mass is obtained, the solid portions of which melt with decomposition at 200 — 220° . Both solid and liquid have a very strong odour.

The hydrocarbon, $C_{10}H_{12}$, at once combines with bromine, and yields a liquid bromide, which, however, soon decomposes, even in a freezing mixture, and instantly on warming, yielding hydrobromic acid and a black resin. Nor could any oxidation product be obtained, the hydrocarbon being apparently completely burnt on treatment with permanganate or chromic acid. Nitric acid dissolves the crystals easily, and the addition of water to the solution throws down an amorphous nitro-compound, but the quantity obtained was insufficient for an analysis.

In order to attempt to trace the genesis of this solid hydrocarbon, I had recourse to my friend, Mr. Josiah Hardman, who, through his chemist, my former pupil, Mr. Irwin, kindly provided me with about 200 litres of the first runnings from 240 tons of tar. This product was carefully distilled, and about 2 litres of liquid boiling below 30° collected. Of this, 200 c.c. was distilled on April 16, the whole boiling below 30° , and leaving no solid residue. On again distilling this portion, which had been at once sealed in a tube nearly filled with the liquid, about 60 c.c. boiled above 30° , and a solid crystalline residue, weighing about 2 grams, was left behind. This substance melted at 30° , and proved to be the hydrocarbon $C_{10}H_{12}$.

100 c.c. of another portion of the volatile mixed hydrocarbons obtained from a second sample of the first runnings, was distilled on March 7th. It all came over between 30° and 40° , and no trace of solid crystals was noticeable. On April 13th, the liquid contained a high boiling constituent, and the residue yielded crystals of $C_{10}H_{12}$. On repeating the operation on May 5th the thermometer rose to 75° , and crystals were again obtained from the residue. The fraction of this last portion boiling from 20° to 30° was then sealed up until June 29th, when it was again distilled, and from it a small quantity of the crystals was obtained. A third portion of the volatile hydrocarbon from a different tar also exhibited the same behaviour; when first distilled it all came over below 30° , and gave no indication of the

presence of the solid hydrocarbon, but after remaining in a sealed tube for six weeks the thermometer ran up to 65° , and the last drops of distillate yielded the crystalline substance. Hence there can be no doubt that these volatile hydrocarbons do polymerise spontaneously at the ordinary temperature, and that the solid $C_{10}H_{12}$ is, probably, the final product.

To identify the volatile hydrocarbon or hydrocarbons which yield the solid substance proved no easy matter. In order to separate the acetylenes, the most volatile product obtained was shaken up with an ammoniacal silver nitrate solution. The light yellow precipitate obtained, consisted mainly of the silver compound of ethylacetylene, as its molecular weight was found to be 164.3 and 158.7 instead of 161. Portions of the mixture of hydrocarbons thus freed from the acetylenes were distilled on March 4th, and the whole distilled over at 30° , and showed no trace of crystals. It was then allowed to remain as described, until April 9th, when the liquid was found to yield the same solid body. Hence it appears that hydrocarbons, not acetylenes, are capable of spontaneous polymerisation. For the purpose of separation, these non-acetylene hydrocarbons were brominated. The fraction boiling below 30° yielded a large crop of a well crystallisable bromine compound, which on analysis proved to be butine tetrabromide, $C_4H_6Br_4$, the percentage of bromine obtained being 85.7 and 85.3, as against 85.6 required.* Amylene dibromide, boiling at $170-180^{\circ}$, and giving a percentage of 70.0 of bromine as against 69.56, was also obtained in quantity. A liquid pentene tetrabromide, $C_5H_8Br_4$, also occurred amongst the numerous brominated derivatives. This was distilled in a vacuum, and yielded on analysis 81.83 per cent. of bromine, as against 82.47 per cent. The sp. gr. of this bromide was 2.37. Whether, as seems not unlikely, the new crystalline hydrocarbon is derived from a hydrocarbon, C_5H_8 , an isomeride of valylene, must at present remain doubtful, as the search for this body proved unsuccessful.

* The melting point of this tetrabromide was 116° ; that of Helbing's was 99° . (*Annalen*, 172, 281.)

LXXI.—*On the Non-existence of Gaseous Nitrous Anhydride.*

By WILLIAM RAMSAY, Ph.D., and J. TUDOR CUNDALL.

IN a recent communication to the Society, Dr. Lunge has, very naturally, defended his view that nitrous anhydride is capable of existence in a gaseous state, but in doing so he accuses us of almost every sin of which chemists are capable. In bringing forward a fresh proof of the non-existence of gaseous nitrous anhydride, we may be excused if we take this opportunity of replying to his criticism.

Dr. Lunge states, first, that we do not acknowledge his priority in ascertaining the composition of the products of the action of nitric acid of different degrees of concentration on arsenious anhydride. When we remark that "it is commonly believed that the indigo-blue or green liquid produced by the action of arsenious anhydride on nitric acid has the formula N_2O_3 ," we merely quote the opinion usually stated in text-books, and we regret that we have appeared to include Dr. Lunge amongst those who share this belief.

In mentioning the various methods attempted for the analysis of these oxides of nitrogen, we merely did what we considered to be desirable, namely, not omit to mention unsuccessful attempts. As long ago as 1873, one of us made use, in the laboratory of Anderson's College, Glasgow, of an extemporised "nitrometer" precisely similar to that introduced by Dr. Lunge; but such a nitrometer would not have answered our purpose, for it was necessary to introduce a bulb to measure the gases under reduced pressure and to secure equality of temperature; and as nitric peroxide at once attacks grease, the use of a stopcock was inadmissible. Moreover, the apparatus we employed was not so cumbersome as Dr. Lunge appears to think, and it suited our purpose well, which was to obtain the vapour-density of the portion of substance of which the analysis was made. It may here be remarked that there was no difficulty in bringing the gases completely into contact with the mercury and sulphuric acid: for by closing the tube with the thumb, it may be removed from the trough and shaken until the mercury is divided into a grey powder.

Now, as regards the incorrectness of our results. Everyone who has tried knows the difficulty of filling small bulbs with a liquid boiling (or decomposing) at a temperature below 0° . We are, therefore, willing to admit that the various samples of blue liquid collected about -20° were altered more or less in composition during the filling of the bulbs; this we believe accounts, at least to some extent, for the differences in the results of analyses of the nine samples mentioned

as batch F* (this vol., p. 192). It was therefore thought more trustworthy to take the mean of those analyses in calculating the composition of the mixture, than to treat each analysis on its own merits.

It will be noticed, however, that although, as Dr. Lunge justly points out, there are discrepancies between the vapour-densities found by us and those calculated by help of Professor Willard Gibbs's formula, yet the calculated densities are, in every case but one, somewhat higher than those found by us; and this certainly points in favour of the theory of the complete dissociation of gaseous nitrous anhydride.

As regards Dr. Lunge's own very complete researches, we agree with a remark made by Dr. Armstrong during the discussion which ensued on the reading of our paper:—that evidence drawn from the behaviour of nitric oxide or nitrous anhydride (?) towards oxygen in presence of a third reacting substance can carry no conviction as to the composition of the mixture of reacting oxides. Dr. Lunge asserts (*Ber.*, 1879, 358) that NO and O₂, when mixed, *must* unite completely to form NO₂ + N₂O₄. Is this, however, proved beyond doubt? It may be contended that a mixture of NO and O₂ need not unite wholly to NO₂ + N₂O₄; but that, whilst a certain amount of combination occurs, it is not necessarily complete. It is well known that the presence of a product of reaction tends to prevent complete combination of reacting substances; and there is no proof that such incomplete combination does not take place in the experiments lately described by Dr. Lunge (*Ber.*, 1885, 1384, *et seq.*). His analyses may have shown that NO with excess of O₂ gives partially N₂O₄ + NO₂, but his method of analysis is one which removes that product of the reaction, and would not affect the excess of oxygen. Without entering into detailed criticism of Dr. Lunge's experiments, let us here point out the unique behaviour of Dr. Lunge's gaseous N₂O₃, inasmuch as although, according to him, it dissociates, yet the extent of dissociation is not increased by a rise of temperature; in fact, if the temperature be raised from 3.5° to 153° no increase of dissociation of this dissociable body is observable! (*Ber.*, 1879, 359, par. 3.)

As regards the existence of a gaseous nitrous anhydride, we still hold with the majority of chemists that the density of a gas is the best evidence, if not the only one, of its molecular formula; and although exception may be taken on several grounds to our experiments, yet the following experiment appears to us decisive. The principle of this experiment was originally devised by Than (*Annalen*, 131, 199) for the purpose of ascertaining whether contraction was noticeable on mixing ammonia and hydrogen chloride at a high temperature. A tube about 600 mm. long and 10 mm. in diameter was

sealed at one end, and the glass was blown out so that it could easily be broken by a shock. This tube was filled with dry mercury and inverted in a mercury trough. Another tube of about 15 mm. in diameter and 560 mm. in length was constricted at one end, so that it could be easily closed at the constriction by a blowpipe flame. In the wider tube was placed a small sealed glass bulb, with a long thin stem, containing pure peroxide, which had previously been distilled from and over phosphoric anhydride, and the wider tube was carefully slipped over the narrower tube so that the bulb occupied the space between the two tubes, as shown in the woodcut. The constricted



part of the wider tube was then attached to an air-pump, and when the air was removed, mercury ascended until it reached the constriction in the wider tube, the open end of which dipped under the surface of the mercury in the trough. The constricted portion was then sealed. By moving up the inner tube, the stem of the bulb containing nitric peroxide was broken, the peroxide boiled into gas, and the mercury immediately fell to a certain level between the two tubes. Nitric oxide, dried by passage through phosphoric anhydride, was then passed up the inner tube, until the mercury in both tubes had the same level. By pressing on the wider tube, the top of the inner tube was easily broken; but on doing this *no alteration in the level of the mercury was observable.*

Now, if combination between NO_2 and NO had occurred, a contraction from two volumes to one should have taken place; and if $\text{N}_2\text{O}_4 + 2\text{NO}$ had reacted, a contraction from three volumes to two: as nitric peroxide gas is a mixture of the two gases NO_2 and N_2O_4 in certain proportions, total combination with NO would have caused some contraction intermediate between these two proportions.

The top of these tubes was then surrounded with a freezing mixture of hydrochloric acid and ice; a quantity of dark blue liquid formed on the side of the outer tube, and trickled down its walls;

on reaching the warmer space, it was at once reconverted into red gas. On removing the freezing mixture, and allowing the tube to stand for some hours, the mercury regained nearly its original level, the total contraction being about 2 per cent. of the total original volume of the gas. This contraction is to be explained, we think, by the fact that when the mercury rises in the tube, a fresh surface is constantly exposed, which becomes covered with a white film, probably consisting of nitrate. Hence the action of nitric peroxide on mercury is attended by contraction, as observed by Naumann, and not by expansion, as supposed by Dr. Lunge. So long as the surface of the mercury is protected by a film there is no action, and no contraction is observable. Even were it to be ascribed to combination between $N_2O_4 + NO_2$ and NO , it is very small in amount; and we think that the above explanation is to be preferred, in view of the evidence previously obtained, that no contraction is observable on mixing the gases.

But Dr. Lunge will reply that the act of combination of $N_2O_4 + NO_2$ with NO is a very slow one, and, indeed, he has stated that to be the reason why we could not obtain a liquid with a higher percentage of N_2O_3 than 31.3, whereas, according to him, by using nitric acid of appropriate strength, nearly pure N_2O_3 may be obtained, and distilled off with little decomposition in the gaseous state. Now it is true that the time occupied in the dissociation of dissociable bodies into their components, or conversely of union of those components into their compound, is longer the lower the temperature; but it is equally true that union always takes place comparatively quickly at first, and it is that union expressing equilibrium which always demands a long time. And if gaseous N_2O_3 be capable of existence at all it must be present in a mixture of $(N_2O_4 + NO_2)$ and NO at any given temperature (provided time sufficient for combination be allowed), in the same proportion as it would be were gas obtained from the liquid N_2O_3 , kept at the same temperature, during a sufficient length of time. It would be a conclusive proof in favour of the existence of gaseous N_2O_3 , were it to be shown that a mixture of nitric peroxide with nitric oxide in such proportion as to form nitrous anhydride, had, shortly after mixing, a vapour-density different from that of the first portions of the distillate from the blue liquid, however obtained, since in the one case, according to Dr. Lunge's own showing, incomplete combination should ensue, and in the other incomplete decomposition. Now, the fact that no immediate contraction occurs on mixing the gases is a sufficient proof that combination, if it takes place at all, is very slow. We have made experiments, of which an account will now be given, which prove that decomposition is very rapid.

Mr. Groves having found that acid of 1.3 sp. gr. in contact

with arsenious oxide at a temperature of 70° gave the product richest in N_2O_3 , we prepared by this means a dark-blue liquid, which, as usual, was dried by passing its vapour over phosphoric anhydride. It was collected in a double-necked bulb, and until required was sealed up. To ascertain the specific gravity of the gas obtainable from this liquid, a bulb of 860 c.c. capacity was used, having a very narrow neck closed by a piece of thick india-rubber tubing and a clip. It was completely exhausted by means of a Sprengel's pump and weighed. This india-rubber tubing was slipped over one of the outlet tubes of the bulb containing the blue liquid, wired, and the point of the tube then broken off. The clip was then opened, and the vacuum flask became filled with red gas. The bulb was heated with the hand until a small gauge which could be connected at will showed an excess of pressure over the atmospheric. The clip was then closed and the bulb removed, and the bulb containing the blue liquid was then cooled and sealed. During the filling the large bulb was kept at a constant temperature by being immersed in a large trough of water. While in the bath the clip was opened to reduce the pressure to that of the atmosphere; it was then immediately closed, and the bulb was weighed. The whole operation of introducing gas took less than three minutes, so as to allow as little time as possible for dissociation. After weighing the bulb, a glass tube was inserted into the india-rubber tube, and dipped under strong sulphuric acid. On opening the clip and cooling the bulb, acid entered and absorbed the gases. When the gas became colourless the clip was opened and air admitted. In the earlier experiments a red colour was noticeable, showing the presence of uncombined NO. This red gas having been absorbed, the sulphuric acid was then transferred to a weighed flask, and the bulb was rinsed out several times with pure sulphuric acid containing no nitric acid, and the rinsings added. The total weight of acid was then ascertained, and fractional portions taken for analysis by means of a nitrometer. In spite of Dr. Lunge's recommendation, it was useless to estimate oxygen with permanganate, for, as was before remarked, red fumes accompanied the admission of air; and the addition of air was necessary, in order that all the nitrogen should be absorbed.

The results are as follows :—

First Fraction.

Weight of oxide..... 1.6136 grams.
 Total weight of acid..... 159.1765 „

	(1.)	(2.)	(3.)	(4.)
Weight of acid taken.....	5.4037 grams	5.2028 grams	5.1695 grams	4.5365 grams
Volume of nitric oxide.....	34.08 c.c.	34.28 c.c.	33.18 c.c.	28.98 c.c.
Temperature....	20.5°	21.1°	20.6°	22.8°
Pressure, corrected at 0° ..	754.9 mm.	754.5 mm.	754.5 mm.	754.9 mm.
Corrected volume of NO	31.48 c.c.	31.59 c.c.	30.64 c.c.	26.57 c.c.
Weight of nitrogen.....	0.01974 gram	0.01981 gram	0.01922 gram	0.01667 gram
Nitrogen in total acid	0.58121 „	0.6062 „	0.5917 „	0.5848 „

Mean percentage of N..... 36.63

Percentage of N in N_2O_3 36.84

This gas has therefore approximately the composition N_2O_3 . The volume of the bulb being known, the vapour-density was easily calculated. It was found to be 22.35 at a temperature of 18.2° and a pressure of 759.5 mm. Calculating by means of Professor W. Gibbs's formula, the theoretical density of a mixture of $NO_2 + N_2O_4$ with NO of the composition entailed by the above analyses at 18.2° and 759.5 mm. is found to be 23.42—somewhat greater than that found by us. It is noticeable that this result is confirmatory of our previous experiments, and also of a number of experiments on the density of pure N_2O_4 , no diluting gas being present; in these cases the density found was invariably lower than that calculated by means of Professor Gibbs's formula.

Dr. Lunge says that N_2O_3 volatilises with slight decomposition. Now, if the gas of which we determined the density be supposed to contain no N_2O_4 , but only NO, NO_2 , and N_2O_3 , the percentage of N_2O_3 necessary to be added to raise the specific gravity of $(NO + NO_2)$ to 22.35 would be 17.63. If N_2O_3 therefore be present at all, it is impossible that more than 17.63 per cent. has escaped decomposition during volatilisation, and it appears much more probable, indeed certain, that this must be ascribed to the usual cause, the existence of N_2O_4 in the gaseous mixture.

Dr. Lunge states that the blue liquid obtained by him is in many cases nearly pure N_2O_3 . It is, of course, impossible to assume the identity of our sample with his, but it may be interesting to give the

results of analyses and vapour-densities of the subsequent fractions of our stock.

Fraction.	Percentage of N.	Density.	Remarks.
2	35.45	24.72	After absorption with sulphuric acid, slight red colour on introducing air.
3	33.59	26.26	Very slight red colour with air.
4	32.18	31.19	No coloration.
5	31.32	36.03	No coloration.

The blue colour of the liquid turned gradually to green, and the residue had an olive tint.

The argument then stands thus:—On mixing NO and ($\text{N}_2\text{O}_4 + \text{NO}_2$) no contraction ensues, even after standing for some time: therefore, if combination occurs at all, it must occur very slowly. On distilling a liquid containing N_2O_3 , the first portion of the distillate has the empirical composition N_2O_3 , but is proved by its density to contain at most 17.63 per cent. of undecomposed N_2O_3 ; and this on the assumption which is known to be false, that no N_2O_4 is present in the gaseous mixture. It cannot, of course, be concluded that no N_2O_4 is present in the gaseous state, but the near coincidence of the found density with that calculable by Professor Gibbs's formula is a strong presumption that gaseous N_2O_3 is absent, and, indeed, is incapable of existence. Taken in conjunction with the remarkable behaviour of the supposed gaseous N_2O_3 , the dissociation of which, as already mentioned, was found by Dr. Lunge to be uninfluenced by temperature, we regard the proof as conclusive.

In conclusion, we would remark that, contrary to Dr. Lunge's statement, we do not find that NO is slowly and quite incompletely absorbed by liquid N_2O_4 . The rate of absorption is rapid, and its amount greater the lower the temperature.

Again, it appears quite as conceivable that $\text{NO}_2 + \text{NO}$ act simultaneously on absorbing agents, as that they must first combine before action is possible.

The sole result of Dr. Lunge's experiments appears to us to be the proof that nitric oxide and oxygen can exist in presence of a large amount of peroxide without combination. We have found that below a red heat nitric peroxide becomes colourless, implying dissociation into NO and O_2 , and it is quite possible that in presence of a large excess of the product, nitric peroxide, the constituents nitric oxide and oxygen should remain uncombined, even at the ordinary temperature.

LXXII.—*On some Derivatives of Anthraquinone.*

By A. G. PERKIN and W. H. PERKIN, jun., Ph.D.

DURING some experiments on the sulphonic acids of anthraquinone it was observed that the sodium salts of these acids were decomposed in a somewhat remarkable way when submitted to dry distillation. As the compounds formed appeared to be of considerable interest, we have investigated them more closely.†

The sodium salt employed in the following experiments was the so-called "silver salt" which is produced in such large quantities in alizarin factories, and which consists of nearly pure sodium anthraquinonemonosulphonate.

The specimen used was soluble in water, forming a clear neutral solution, which gave no coloration with caustic soda, and thus showed the absence of hydroxyanthraquinone-derivatives. Dried at 120° and ignited with nitrate of ammonia, 0.2005 gram gave 0.0467 gram $\text{Na}_2\text{SO}_4 = 23.29$ per cent.; calculated for $\text{C}_{14}\text{H}_7\text{O}_2\cdot\text{SO}_3\text{Na} = 22.97$.

The dry distillation of this salt was carried out in an iron tube 8" x 2" welded together at one end. A piece of gas piping, bent at a right angle, was screwed into the aperture of this tube, and its open end passed through a loose wooden lid into a large cylindrical copper vessel which served as a condenser. The retort was charged with about 150 grams of salt, and heated over an ordinary fire. After a few minutes, yellowish-brown vapours were evolved which easily condensed in the receiver, and these continued to come off until the end of the operation, the whole distillation usually occupying about half an hour.

The distillate was a brownish, fluffy mass, mixed with a small quantity of a slightly acid liquid containing sulphur in suspension. On unscrewing the connecting tube it was usually found to contain a small quantity of long yellow needles easily recognisable as anthraquinone.

The yield of distillate was small—on an average only about 20 per cent. of the weight of salt employed. From 55—60 per cent. of residue remained in the retort as a hard, brittle, carbonaceous mass; this, when extracted with water, yielded a strongly alkaline, green solution, which was found to consist almost entirely of sodium sulphide containing a little ferrous sulphide.

The distillate, which proved to be a mixture of several compounds, was digested for some time with boiling baryta-water. A portion dissolved, producing a blood-red solution which was separated from

the insoluble residue by filtration. The filtrate, after standing for some time, was again filtered, and then treated with dilute hydrochloric acid, which caused the precipitation of a small quantity of a straw-coloured, gelatinous substance.

This was thrown on a filter, well washed with water, and dried. After repeated recrystallisation from coal-tar naphtha, it was obtained pure in the form of pale-yellow needles, which on analysis gave the following numbers:—

0.2058 gram substance gave 0.0693 H_2O and 0.5641 CO_2 .

	Found.	Theory: $\text{C}_{14}\text{H}_8\text{O}_3$.
C	74.75 per cent.	75.00 per cent.
H	3.74 ,,	3.57 ,,
O	21.51 ,,	21.43 ,,

It was therefore metahydroxyanthraquinone, the compound produced by fusing anthraquinonemonosulphonic acid or metabromoanthraquinone with potash (Graebe and Liebermann, *Annalen*, 160, 141), and agreed in properties with this compound in every respect. It melted at about 300° (metahydroxyanthraquinone 302°), and gave an easily soluble barium salt (distinction from orthohydroxyanthraquinone).

The residue insoluble in baryta-water was repeatedly extracted with boiling glacial acetic acid, until the extracts became of a pale, yellowish colour. These extracts, when filtered from the insoluble residue and cooled, deposited a dirty yellowish substance, which was separated from the mother-liquors, well dried, and sublimed. The sublimate, which appeared to consist chiefly of anthraquinone, was extracted with small quantities of hot coal-tar naphtha, in order to free it from traces of a more soluble substance, and the residue repeatedly recrystallised from the same solvent. On analysis it gave the following numbers, showing it to be anthraquinone:—

0.1207 gram substance gave 0.0448 H_2O and 0.3554 CO_2 .

	Found.	Theory: $\text{C}_{14}\text{H}_8\text{O}_2$.
C	80.30 per cent.	80.77 per cent.
H	4.12 ,,	3.84 ,,
O	15.58 ,,	15.39 ,,

This compound crystallised in yellow needles, melting at $271\text{--}273^\circ$ (anthraquinone melts at 273°). On heating it in a test-tube it sublimed in the beautiful way so characteristic of anthraquinone, and had, moreover, all the properties of that compound.

On evaporating the mother-liquors from the above crystals they deposited a small quantity of metahydroxyanthraquinone which had

escaped extraction in the first instance. The residue, after having been extracted a few times with glacial acetic acid as described above, was digested with large quantities of glacial acetic acid and filtered, this operation being repeated until the whole was dissolved. On cooling the solutions thus obtained a yellowish-red substance separated out, which under the microscope was seen to consist for the most part of minute crystals. By carefully recrystallising this substance several times from the same solvent, it was obtained pure in the form of a spongy mass of minute reddish-yellow needles, which sometimes had a silky lustre. The greatest care was necessary in order to obtain this substance well crystallised, the method found to give the best results being the following:—A saturated solution in boiling acetic acid was filtered into a flask standing on a sand-bath and containing a small quantity of boiling acid, the funnel being so arranged that the greater portion was heated by the vapour evolved. After filtration the lamp was removed, and the whole allowed to stand in a place free from draught. The separation of the substance, which commenced after several minutes, was peculiar, reminding one somewhat of a fungoid growth. It started at the bottom of the vessel in small spongy tufts which gradually grew until the whole liquid was filled with crystals. If the solution be quickly cooled, or agitated during cooling, the substance is deposited in a more or less gelatinous condition. The following numbers were obtained on analysis, each sample being from a different preparation.

I.	0.1248 gram substance gave	0.0390 H ₂ O and	0.3425 CO ₂ .
II.	0.1745 " "	0.0526 H ₂ O "	0.4815 CO ₂ .
III.	0.1358 " "	0.0420 H ₂ O "	0.3728 CO ₂ .
IV.	0.1415 " "	0.0437 H ₂ O "	0.3899 CO ₂ .
V.	0.1354 " "	0.0418 H ₂ O "	0.3740 CO ₂ .

	Found.						
	I.	II.	III.	IV.	V.	C ₂₈ H ₁₄ O ₆ .	C ₁₄ H ₈ O ₃ .
C..	74.84	75.25	75.19	75.16	75.33	p. c.	75.34 75.00 p. c.
H...	3.46	3.35	3.43	3.29	3.43	"	3.14 3.57 "
O..	21.70	21.40	21.38	21.55	21.24	"	21.52 21.43 "

This compound therefore appears to have the formula C₂₈H₁₄O₆, rather than that of C₁₄H₈O₃, which is also borne out by its properties. It is practically insoluble in all the usual solvents in the cold, and only very sparingly soluble in boiling acetic acid, from which it seems to crystallise best. For ordinary purposes it is therefore only necessary to extract the crude product from the destructive distillation of the sodium anthraquinonemonosulphate with alcohol or acetic acid

until the more soluble portion has been removed, and to use for further reactions the sparingly soluble residue, which consists of the compound $C_{28}H_{14}O_6$ in an almost pure state. On distillation with zinc-dust, the compound $C_{28}H_{14}O_6$ gave anthracene—recognised by its melting point (215°), and from the fact that it gave anthraquinone on oxidation. When heated, it melts at a temperature much above 300° , to a reddish-black liquid, which on further heating sublimes as a reddish powder, only a small quantity of charcoal being left. It dissolves in concentrated sulphuric acid in the cold, forming an intense magenta-coloured solution, from which on the addition of water it is precipitated unchanged in the form of a transparent yellow jelly. When heated to a high temperature with fuming sulphuric acid, it dissolves, forming an orange-coloured solution resembling anthraquinonesulphonic acid, with which, however, it is not identical. At very high temperatures a small quantity of a colourless, crystalline sublimate was obtained. This readily dissolved in a hot solution of sodium carbonate, and on addition of acid, extraction with ether, and evaporation of the ethereal extract, colourless needles were obtained, which were easily recognised as phthalic acid.

A boiling mixture of nitric and sulphuric acids dissolves it, and on addition of water a white substance is precipitated, which separates in an amorphous condition from its boiling solution in ordinary solvents. The compound $C_{28}H_{14}O_6$ is, curiously enough, absolutely insoluble in alkalis. When fused with caustic soda it dissolves, forming a violet mass, which has the properties of sodium alizarate, and which, on solution in water and treatment with acid, gives a yellow precipitate; this dyes mordanted cloth in a way perfectly analogous to alizarin.

As it was important to be sure of the formation of alizarin, a quantity of the red body was heated with a strong solution of caustic soda in an iron tube at 180° , and the sodium alizarate, after dilution with water and filtering, purified by conversion into the lime salt. On acidifying this salt with hydrochloric acid, a yellowish mass was precipitated, which after being collected, well washed with water, and recrystallised, was found to melt at 277° (alizarine melts at 275°). The identity of these two substances was further proved by the similarity of the spectra of their solutions.

Heated with zinc-dust and caustic soda the compound $C_{28}H_{14}O_6$ dissolves, and forms a blood-red solution, which on exposure to the air is decolorised, the original compound being reprecipitated. In this respect the substance very much resembles anthraquinone.

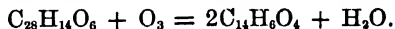
Oxidation of the Compound $C_{28}H_{14}O_6$.

If a boiling saturated solution of this substance in glacial acetic acid be treated with chromic acid, a violent reaction sets in, and, on cooling, a whitish substance separates. As it was thought that the examination of this reaction might give some clue to the constitution of the compound $C_{28}H_{14}O_6$, it was carried out on a large scale in order to obtain the white substance in sufficient quantity for analysis. For this purpose the boiling solution of the red compound was treated with chromic acid, in small quantities at a time, until it was no longer reduced. The boiling was then continued for a short time, and the solution allowed to cool. After standing for some hours, the green solution had deposited a quantity of a white crystalline substance, which was collected, well washed with water, and dried at 100° . After being purified by several crystallisations from coal-tar naphtha, it was obtained in the form of colourless transparent plates melting at $292\text{--}295^\circ$. On analysis the following numbers were obtained:—

- I. 0.1546 gram substance gave 0.0439 gram H_2O and 0.3988 gram CO_2 .
 II. 0.1196 gram substance gave 0.0327 gram H_2O and 0.3096 gram CO_2 .

	Found.			Theory.
	I.	II.		$C_{14}H_6O_4$.
C	70.35	70.59	per cent.	70.59 per cent.
H	3.15	3.03	„	2.52 „
O	26.50	26.38	„	26.89 „

The compound has therefore the formula $C_{14}H_6O_4$, and is formed from the compound $C_{28}H_{14}O_6$ according to the equation—



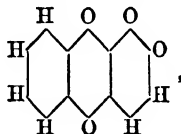
It is almost insoluble in boiling benzene, slightly soluble in boiling coal-tar naphtha and acetic acid, more soluble in boiling aniline; on cooling, it separates from the latter, in the form of transparent needles. It is quite insoluble in alkalis, and can therefore contain no hydroxyl-group.

When heated it first melts to a straw-coloured liquid, and then sublimes almost without decomposition. It yields anthracene when distilled with zinc-dust. On warming with phenylhydrazine it yields a red substance, which, however, has not been obtained in sufficient quantity for analysis. The hot alcoholic solution of the compound $C_{14}H_6O_4$ gives, on the addition of ferric chloride, a reddish-brown coloration. When heated with strong alcoholic potash, a violet solution is first

obtained, which, however, again becomes colourless on shaking with air. If the heating be repeated, a reddish-brown solution is obtained.

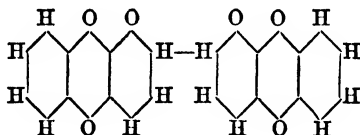
If the substance is heated with aqueous potash and a trace of zinc-dust, a violet solution is produced, which on the addition of more of the reducing agent changes to olive-green. On agitating with air, the solution becomes first violet and then colourless, the original compound being reprecipitated. With zinc-dust and ammonia a violet solution is produced, which becomes colourless in contact with the air.

From the study of these properties, it seems that the compound $C_{11}H_6O_4$ must have the following formula:—



it being an orthoquinone of anthraquinone.

The red substance $C_{22}H_{14}O_6$ has therefore probably the constitution—



being a derivative of di-anthracene.

These formulæ, however, require further experimental proof before they can be looked upon as being definitely settled. It is also intended to investigate the behaviour of the α - and β -salts of anthraquinone-disulphonic acid when submitted to dry distillation.

LXXIII.—*Researches on the Relation between the Molecular Structure of Carbon Compounds and their Absorption Spectra.* (Part VII.)

By W. N. HARTLEY, F.R.S., Professor of Chemistry, Royal College of Science, Dublin.

Introduction.

IN a paper published in the *Journal of the Chemical Society*, 39, 153, 1882, I have given an explanation of the cause of the absorption-bands occurring in the spectra transmitted by various carbon compounds and tertiary bases; and I have also calculated the approximate mean rate of vibration of the molecules of these substances from observations on their absorption spectra. It was shown that such substances as we designate closed-chain compounds are characterised by two kinds of absorption—a general and a selective absorption—the latter not independent but a result of the former. The general absorption was considered to be due to the fundamental vibrations of the molecule, the selective absorption being caused by vibrations within the molecule corresponding to the overtones of a simple musical instrument such as a stretched string or a bell. Intimately connected with the rate of these vibrations and the chemical constitution of the molecule, is the intensity of the absorption; this was attributed to the amplitude of the vibrations.

No measurements of the wave-length of the lines occurring in ultra-violet spectra had at that time been made in sufficient number and with the accuracy necessary to afford a means of measuring these bands in a satisfactory manner; but since then many lines have been measured in the spark spectra of various elements by my assistant Mr. Adeney and myself, and consequently I have been enabled to place definite measurements of these bands on record. The method of working is that described in the *Proc. Roy. Soc.*, 33, 1 (Abstract).

The wave-lengths in tenth-metres have been converted into reciprocal numbers which have the advantage of representing oscillation-frequencies per unit of time; for inasmuch as we assume that only those rays are absorbed by a substance which synchronise with the vibrations of the molecule, there is a very obvious connection between the molecular vibrations and the oscillation-frequencies of the absorbed rays. The quantity of substance taken in each case is a molecular weight in milligrams; this is dissolved in a diastinic medium and made up to a constant volume, definite thicknesses of the solution being examined. That is to say, a milligram-molecule is contained in, or, more correctly, an equal number of molecules are

diffused through unit of space. The oscillation-frequencies being taken as abscissæ and the thicknesses of liquid as ordinates, absorption curves are plotted which record the rate and amplitude of the molecular vibrations. The area enclosed by the curve is a description of the specific absorptive power of a substance, and it follows that as all the properties of a molecule are dependent upon its mode of vibration, each substance has its own peculiar curve by which it may be identified.

From the usual point of view of the chemist, it might be considered as open to discussion whether molecules identical in composition and of similar constitution would or would not yield different absorption-curves, for if the bands caused by selective absorption are the result of motions within the molecule, these are motions of the atoms of which it is composed, and, consequently, the distinctive properties of the atoms which are common to each molecule should be made manifest by distinctive series of vibrations indicated by similar curves.

To this we have an answer in the fact that it has already been proved (*Phil. Trans.*, 170, 257, 1879) that the curves of some few isomeric bodies are widely different, and in no case can any so-called atomic motions be traced, or, as I have elsewhere stated, it is not possible to associate any of the absorption-bands of the aromatic hydrocarbons with any particular carbon-atoms; indeed it was shown that vibrations of the molecule, as a whole, determine the rate of the vibrations taking place within the molecule. Here then we have evidence of the constitution of matter which is inconsistent with the individual existence of atoms within the molecule; and it appears from this consideration alone that our chemical formulæ do not in any way express the constitution of the molecules of the substances they are intended to represent, but only give us a concise and useful statement of the origin of the substance and the chemical reactions which it is probably capable of undergoing, or to which it has been subjected; all such statements being referred to mass.

Each molecule appears to be a distinct individual resolvable into other individuals, it is true, but not composed of them in the manner represented by symbols.

It is considered desirable thus to preface this paper in order that the object to be studied may be kept clearly in view.

The substances which have been investigated, and the spectra of which are described in these pages are the following:—

1. Aromatic hydrocarbons, benzene and naphthalene.
2. Aromatic tertiary bases and their salts, pyridine, dipyridine, picoline, quinoline, and their hydrochlorides.
3. Addition-products of tertiary bases and salts, piperidine, tetrahydroquinoline and its hydrochloride.

4. Primary and secondary aromatic bases or amido-derivatives and salts thereof, ortho- and para-toluidine and their hydrochlorides.
5. Isomeric bodies, the three isoxylenes.

The Preparation of Solutions and Method of Examination.

In dealing with a variety of nearly related substances from which similar solutions have to be prepared, it is necessary that the least soluble shall, as far as possible, serve as a standard for the preparation of the other solutions. It was found most convenient to take a molecular weight in milligrams and dissolve it in 20 c.c. of absolute alcohol or any other menstruum better suited to the particular substance. In this way, molecular weights were distributed through—that is to say, made to occupy equal volumes. The solutions when prepared were placed in a series of cells varying in thickness from 25 mm. to 1 mm.; if with a thickness of 1 mm. absorption-bands were still visible, the liquid was diluted to five times its original volume and another series of photographs taken ranging from 5 mm. downwards. An example or two will illustrate the method of making and examining the solutions.

The solution of benzene was made by dissolving 0.078 gram in 20 c.c. of alcohol; it was examined in layers 25 mm. in thickness which were reduced gradually to 1 mm.; but below this it was necessary to dilute the liquid, and, therefore, 5 c.c. were made up to 25 c.c.; this is in the proportion of 1 milligram-molecule in 100 c.c. The proportional thickness of 1 mm. of the weaker solution is $25 \times 5 = \frac{1}{125}$ of the whole or of the original solution. In the case of paratoluidine we have a solution containing 0.107 gram dissolved in 20 c.c. of alcohol; examined first in layers of 5 mm. thickness reduced to 1 mm., the solution is then diluted to five times its original volume for a first, a second, and a third time, so that the proportional thicknesses are represented by $5^{-4} = \frac{1}{625}$ mm. diminishing to 1 mm.

In the case of the bases and their hydrochlorides, the method of examination consisted in photographing the spectra transmitted by the base contained in one series of cells and the molecule of hydrochloric acid contained in another, the rays from the spark passing through both simultaneously. The contents of the two series of cells being then mixed and returned to their original vessels, a second series of photographs was taken. As the hydrochloric acid proved perfectly diactinic the first spectra represent the absorption caused by the base alone, the second that caused by the salt. The difference in the mode of vibration of the base, the acid, and the salt is very striking; the amplitude of the vibrations within the molecule of the

salt being much less, as one would imagine, than in that of the base. When a series of photographs had been secured which gave sufficient information from which a curve could be drawn indicating both the general and the selective absorption, the oscillation-frequencies of the absorbed rays were taken as abscissæ and the proportional thicknesses in millimetres of the weakest solution as ordinates. The curves are made continuous, and a careful description of the spectra obtained by transmitting rays through varying thicknesses of the solutions is intended to supplement the curves and serve the purpose of the shaded diagrams hitherto employed. The scale upon which these curves have been drawn is as small a one as possible, but owing to the extraordinary persistence of the bands of absorption occurring in the spectra of certain substances—such as, for instance, the paratoluidine and its hydrochloride—the diagrams are occasionally of such an unmanageable length, as much as 7 feet, that it has been found necessary to break the curves, and to reduce the scale upon which they have been drawn; unfortunately under such circumstances it is difficult to institute strict comparisons between all the substances examined.

The same difficulty in representing the spectra on a uniform scale was experienced when solutions containing equal quantities of substance were employed; this may be seen by referring to this Journal, 39, 153, and comparing the diagram of benzene with that of anthracene. It is possible that in these latter investigations bands of little intensity may have escaped observation, because the method of examination necessary in order to obtain accurate measurements does not admit of the recognition of very feeble bands or such as only occur through a small range; that is to say, which correspond to vibrations of small amplitude. The photographs taken on former occasions which were referred to the spectrum of cadmium, were taken with a wide slit and lenses of long focus; these were executed with a narrow slit and lenses of shorter focus. The latter method was convenient for ascertaining the exact position of the absorption-bands, but it has resulted in the inadequate representation of some feeble bands of absorption and their omission from the curves. The reason of this will be evident when we consider that line spectra consist of *maxima* and *minima* of intensity of chemical action with the most rapid transitions from one to the other when the lines are very clearly defined; but when the slit is open the width of the spark itself and its irregular motion cause the chemical action to be more equally diffused. When *maxima* of chemical action occur in a region of the spectrum where there is only a faint absorption, the effect of absorption is overpowered.

Probably this defect in working with spark spectra could be over-

come by the use of an arc light, but, unfortunately, I have not had such a means of research at my disposal.

The Substances Examined.

Benzene.—The observations made on benzene were numerous, but no difference was observed in the photographs obtained from different specimens; as a matter of fact, however, that preparation which afforded measurements from which the curve was drawn, was fractionated from a supply of crystallisable benzene free from thiophene, supplied by Mr. Kahlbaum's agents. It was analysed and found to give numbers agreeing with theory.

Naphthalene.—Three specimens of naphthalene have been examined at different times, two of these were carefully purified in my laboratory, and their purity ascertained by analysis. These afforded spectra identical in every particular.

Pyridine.—This specimen was fractionally distilled from a preparation obtained from Mr. Kahlbaum; its boiling point lay between 115° and 117° . It was converted into a platinum salt, and two analyses were made, which yielded the same numbers, namely, 17.68 per cent. of nitrogen.

	Found.	Calculated.
Platinum in $(C_5H_5N, HCl)_2PtCl_4$..	34.52	34.60
Nitrogen in " ..	4.89	4.90
Nitrogen in C_5H_5N	17.68	17.72

Picoline.—For this specimen, I am indebted to Professor Ramsay, of Bristol. It was considered to be a pure preparation.

Quinoline.—Two specimens of quinoline have been examined, one of which was described in this Journal, 41, 47; its boiling point ($235-240^{\circ}$) and the particulars of its analysis are there stated. The second specimen was prepared synthetically in my laboratory, after Skraup's process (this Journal, 40, 919). The proportions of the materials used were nitrobenzene 1.4 parts, aniline 2.1 parts, glycerine of 1.26 sp. gr. 6 parts, and sulphuric acid 5 parts. The mixture gave no very energetic reaction at first, but after heating for several hours to 130° , and not higher than 140° , the contents of the vessel entered into most violent ebullition. Nearly the whole of the base produced by this method boiled at 235° (uncorr.). The absorption curve which it yielded was identical with that obtained from the carefully purified specimen obtained from Mr. Kahlbaum, which was previously used. According to Hoogewerff and van Dorp (this Journal, 44, 89), the identity of quinoline from cinchonine, with the base from coal-tar has been established. The former is said to boil at 238.25° to 239.25° , and the latter at 239.25° to 240.25° . De

Coninck (this Journal, 44, 88), gives the boiling point of quinoline from cinchonine as 236—237° at a pressure of 775 mm., that obtained by synthesis, according to Skraup and Koenigs, boils at 228°, while according to Baeyer and others, it is 232°. Certainly the number given as the boiling point of my specimen is nearer to this last.

Piperidine (Kahlbaum).—A fraction boiling from 104—105° was converted into a platinum salt, and two analyses were made by Mr. W. P. Sharpley, Associate of the Royal College of Science. The following figures show the result:—

	Found.	Calculated.
Platinum in $(C_5H_{11}N, HCl)_2PtCl_4$..	33.49	33.89 per cent.
Nitrogen in " ..	4.75	4.80 "
Nitrogen in $C_5H_{11}N$	16.36	16.47 "

Tetrahydroquinoline.—The base was prepared by myself from a specimen of the hydrochloride obtained from Mr. Kahlbaum. Its boiling point was between 240° and 250°. The hydrochloride yielded the following numbers:—

	Found.	Calculated.
Platinum in $(C_9H_{11}N, HCl)_2PtCl_4$..	29.00	28.28 per cent.
Nitrogen in " ..	4.026	4.129 "

As the purity of this specimen could not be satisfactorily ascertained by analysis, various fractional distillates were examined with the spectroscope, and as they were found to yield the same spectra, it was considered that there was no impurity present in quantity sufficient to affect the spectrum.

Orthotoluidine (Kahlbaum).—This specimen was fractionated, and found to boil almost entirely at 197—197.5°.

Paratoluidine (Kahlbaum).—This substance, which was prepared from a quantity of the base obtained five years since, consisted of very fine colourless crystals in a state of very great purity. It had been carefully preserved as a typical specimen.

The three Xylenes (Kahlbaum).

Orthoxylene, b. p. 145°	} At barometric pressure of 29.883 inches.
Metaxylene, b. p. 139—141°	
Paraxylene, b. p. 139°	

In that portion of my work dealing with the chemical constitution of the alkaloïds ("Absorption Spectra of the Alkaloïds," Part I, *Proc. Roy. Soc.*, 38, 1, Abstract) the absorption spectrum of piperidine was predicted to be quite different from that of pyridine. Whilst the latter gives a strong absorption-band, the former was judged to be capable of absorbing only the more refrangible of the ultra-violet rays without selection of any particular series of vibrations. This

prediction has proved to be quite correct. It was deduced from two of the laws contained in a former series of papers published in 1882 (this Journal, 39, 153, and 41, 45).

No molecular arrangement of carbon-atoms causes selective absorption, unless each carbon is united to the other three carbon-atoms as in the case of benzene.

The simple union of carbon with nitrogen does not cause selective absorption of the ultra-violet rays.

A third deduction here follows, which is a consequence of the observations contained in the latter paper, and is justified by these more recent investigations.

When an atom of nitrogen is substituted for an atom of carbon in the benzene or naphthalene nucleus, the property of selective absorption is still retained.

Piperidine is an addition product of pyridine, a hexahydropyridine in which the carbons and the nitrogen are less compactly united than in benzene and pyridine, and so far resembling in structure benzene hexachloride; it was easy to conclude that as this last body, and others similarly constituted, are endowed with no power of selective absorption, so hexahydropyridine, for a similar reason, would yield a similar spectrum. In forecasting the nature of the spectra transmitted by the addition products of quinoline, such as, for instance, tetrahydroquinoline and its salts, one could not confidently rely on these facts as being sufficient, for although, reading by the light of the information applied to the case of pyridine and piperidine, the substance might reasonably be expected to yield a spectrum with a band or bands of absorption, because five of the atoms of carbon, and the one atom of nitrogen, are condensed to the same degree as in pyridine, yet in addition there are four other carbon-atoms in the molecule less compactly united by reason of the added atoms of hydrogen with which they are combined. These might or might not affect the absorption spectrum. Here it may be as well to state that "the arrangement of atoms in the molecule," an expression which I have used, and shall probably still find it convenient to employ, because it connects these observations with the ordinary symbolic representations of the constitution of chemical compounds, does not refer to any assumed position of the atoms in space, but to the degree of condensation to which the matter composing the molecules has been subjected. That condition, which we may term compactness of structure, usually denoted in the case of carbon compounds by double and treble linking of the carbon-atoms, is more truly expressed by the word "condensation." In the act of combination, the greater the degree of condensation the greater is the quantity of potential converted into actual energy. The greater the amount of actual

energy resulting from the union of the atoms in a molecule, the greater is the specific actinic absorption and the molecular refractive energy, and the less in amount is its heat of combustion assumed to be. It has already been mentioned that the actinic absorption exerted by a molecule may be increased in two directions, first, in that direction which is represented longitudinally on the diagrams, which signifies that the liquid will bear great dilution without its absorptive power being destroyed, although the rays absorbed may be of small wave-length. This indicates that the molecular vibrations are of great amplitude. Secondly, the extent of the absorption may be increased in the direction of the less refrangible rays, which may be explained by the rate of vibration of the molecule being diminished. It is to be observed that the latter generally includes the former, as, for instance, in the case of benzenoid derivatives, especially when the molecule results from the union of two or more benzene nuclei, and more particularly by that mode of condensation which may be described as the fusion of the benzene-rings, as in the case of naphthalene and phenanthrene.

Isomeric Bodies.—Many previous experiments have been directed towards ascertaining by the spectroscope the orientation of isomeric bodies of the aromatic series.

In the paper by Professor Huntington and myself, diagrams show the differences between the three hydroxybenzoic acids and two nitranilines, but as these are oxygenated derivatives possessing far greater absorptive powers than benzene itself, it has been considered desirable to commence an investigation of isomeric hydrocarbons differing as little as possible from benzene, and on this account the three xylenes have been chosen as examples. Free from the complications which the introduction of oxygen into the molecules may occasion in the absorption curves, one may fairly estimate the difference in molecular absorption which is due to nothing more than the so-called relative positions of the compound radicles.

It will be observed that the area enclosed by the curve of meta-xylene appears to be the least, that of the orthoxylene stands next, whilst that of para-xylene is the greatest. Further researches on isomeric bodies are in progress.

Bases and their Hydrochlorides.—It must be remembered that the hydrochloric acid used in each case was perfectly diactinic, but the salt formed, it will be noticed, yields a curve which is distinct from that of the base. Generally speaking, the salts are more diactinic than the bases.

The following deductions may be drawn from this investigation:—

When the condensation of the carbon and nitrogen in the molecule of a benzenoid compound or tertiary base is modified by the addition thereto

of an atom of hydrogen to each atom of carbon and nitrogen, the power of selective absorption is destroyed.

When the condensation of the carbon-atoms in quinoline is modified by the combination therewith of four atoms of hydrogen, the intensity of the selective absorption is reduced, but is not destroyed.

Molecules of compounds, that is to say, molecules composed of dissimilar atoms, vibrate as wholes or units, and the fundamental vibrations give rise to secondary vibrations which stand in no visible relation to the chemical constituents of the molecule, whether these be atoms or smaller molecules.

Hence it appears that a molecule is a distinct and individual particle, which cannot be represented by our usual chemical formulæ, since these only symbolise certain chemical reactions, and fail to express any relation between physical and chemical properties.

The very beautiful researches of Abney and Festing on the absorption spectra of carbon compounds in the infra-red region render one desirous of ascertaining the relation that such spectra bear to those in the ultra-violet.

I have to thank my assistant, Mr. W. R. Barnett, for the care he has taken in measuring the spectra and drawing the curves which illustrate this paper.

Description and Measurements of Spectra.

BENZENE. 0.078 gram dissolved in 20 c.c. of alcohol.

Thickness of layer of liquid	25 mm.		20 mm.		15 mm.	
	Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to	3151	3171	3151	3171	3151	3171
" fairly strong to	3359	2976	3359	2976	3647	2740
" weak to	3647	2740	3647	2740	3803	2629
" faint to	3768	2653	3803	2629	—	—
(1) Absorption band from	3768 to 4331	2653 to 2310	3803 to 3861	2629 to 2589	3803 to 3861	2629 to 2589
• Rays transmitted, discontinuous to ...	—	—	—	—	3890	2568
• Rays feebly transmitted at	4331	2310	3890	2568	—	—
(2) Absorption band from	—	—	3890 to 4331	2568 to 2310	3890 to 4141	2568 to 2415
Rays weak and discontinuous to	—	—	—	—	4427	2259
Rays transmitted at	—	—	4253	2352	—	—
" discontinuous and faint to	—	—	4426	2259	—	—
Thickness of layer of liquid	10 mm. The same as with 15 mm., but a rather stronger spectrum.					

BENZENE—continued. 0.078 gram dissolved in 20 c.c. of alcohol.

• Description of spectrum.	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to	3151	3171	3151	3171	3151	3171
" fairly strong to	3647	2740	3647	2740	3647	2740
" weak to	3826	2613	3826	2613	3826	2613
(1) Absorption band from	3826 to 3855	2613 to 2593	3826 to 3855	2613 to 2593	3826 to 3844	2613 to 2601
Rays transmitted at	3855	2593	3855	2593	3844	2601
Continuous, weak to	3890	2568	—	—	3919	2549
" faint to	—	—	3890	2568	—	—
(2) Absorption band from ..	3890 to 3959	2568 to 2525	3890 to 3959	2568 to 2525	3919 to 3948	2549 to 2532
Rays transmitted at	3959	2525	3959	2525	3948	2532
Continuous, faint to	4016	2490	4016	2490	4028	2482
(3) Absorption band from	4016 to 4038	2490 to 2476	4016 to 4038	2490 to 2476	4028 to 4038	2492 to 2470
Rays transmitted at	4038	2476	4038	2476	4038	2470
Continuous, faint to	4098	2440	4098	2440	4098	2440
(4) Absorption band from	4098 to 4125	2440 to 2424	4098 to 4125	2440 to 2424	4098 to 4120	2440 to 2427
Rays transmitted at	4125	2424	4125	2424	4120	2427
Continuous, faint to	4566	2190	4566	2190	4566	2190

BENZENE—continued. 0.078 gram dissolved in 20 c.c. of alcohol.

Thickness of layer of liquid.....	2 mm.		1 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to	3151	3171	3151	3171
" " fairly strong to	3647	2740	3647	2740
" " weak to	3826	2613	3826	2613
(1) Absorption band from	3826 to 3844	2613 to 2601	3826 to 3844	2613 to 2601
Rays transmitted at	3844	2601	3844	2601
Continuous, weak to	3919	2549	3919	2549
(2) Absorption band from	3919 to 3943	2549 to 2532	3919 to 3948	2549 to 2532
Rays transmitted at	3948	2532	3948	2532
Continuous, faint to	4028	2482	4028	2482
(3) Absorption band from	4028 to 4038	2482 to 2470	4028 to 4038	2482 to 2470
Rays transmitted at	4038	2470	4038	2470
Continuous, faint to	4098	2440	4098	2440
(4) Absorption band from	4098 to 4120	2440 to 2427	4098 to 4120	2440 to 2427
Rays transmitted at	4120	2427	4120	2427
Continuous, faint to	4566	2190	4566	2190

With 1 mm. of liquid the last two bands have become rather diffuse, and definite measurements are difficult. Although the absorption is quite visible, still some rays are transmitted faintly between the measurements given.

The former solution diluted to five times its original volume, or 20 c.c. made up to 100 c.c. = 0.078 gram in 100 c.c.

Description of Spectrum.

5 mm. Exactly the same as with 1 mm. of the original solution.

4 mm. The same; the first two bands are visible, but do not admit of exact measurement, the others have disappeared.

3 mm. The first two bands are still visible.

2 mm. The whole spectrum is continuous.

NAPHTHALENE. 0.128 gram dissolved in 20 c.c. of alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to	3151	3171	3151	3171	3151	3171
" " faint to	3187	3140	3194	3130	—	—
" " weak to	—	—	—	—	3194	3130
(1) Absorption band from	—	—	—	—	3194 to 3228	3130 to 3097.5
Rays transmitted, continuous, but very feeble to	—	—	—	—	3249	3078
(2) Absorption band from	—	—	—	—	3249 to 3297	3078 to 3033
Rays transmitted feebly at	—	—	—	—	3297	3033
Thickness of layer of liquid.....	2 mm.		1 mm.			
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.		
Continuous, strong to	3151	3171	3194	3130		
" " fairly strong to	3194	3130	—	—		
" " weak to	—	—	3207	3117		
(1) Absorption band from	3194 to 3228	3130 to 3097.5	3207 to 3228	3117 to 3097.5		
Rays transmitted at	3249	3078	—	—		
(2) Absorption band from	3249 to 3297	3078 to 3033	—	—		
Rays transmitted at	3297	3033	—	—		
Also very faint line at	3324	3008	—	—		
Weak continuous spectrum to	—	—	3359	2976.5		
Two strong lines at	—	—	3297	3033		
" "	—	—	3324	3008		

NAPHTHALENE—continued. 0.128 gram dissolved in 100 c.c.

Thickness of layer of liquid	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to	3194	3130	3194	3130	3194	3130
" weak to	3207	3117	3207	3117	3207	3117
(1) Absorption band from	3207 to 3228	3117 to 3097.5	3207 to 3228	3117 to 3097.5	3207 to 3223	3117 to 3097.5
Continuous, weak to	3263	3065	3359	2976.5	3359	2976.5
Two strong lines at	3297	3033	—	—	—	—
"	3324	3008	—	—	—	—
(3) Absorption band from	3359 to 3379	2976.5 to 2959.5	3359 to 3379	2976.5 to 2959.5	3359 to 3379	2976.5 to 2959.5
Rays transmitted at	—	—	3379	2959.5	3379	2959.5
Continuous, feeble spectrum to	3399	2942	3399	2942	3399	2942

Thickness of layer of liquid	2 mm.		1 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to	3194	3130	3194	3130
" fairly strong to	—	—	3359	2976.5
" weak to	3207	3117	3439	2906.5
" feeble to	3228	3097.5	—	—
[The absorption here is still plainly perceptible, although the rays are transmitted.]				
Continuous, weak spectrum to	3359	2976.5	—	—
(3) Absorption band from	3359 to 3379	2976.5 to 2959.5	—	—
Rays transmitted at	3379	2959.5	—	—
Continuous to	3439	2906.5	—	—
(4) Absorption band from	3439 to 4259	2906.5 to 2349	3439 to 4125	2906.5 to 2424.3
One very faint line transmitted at	4259	2349	—	—
Rays decreasing in strength to	—	—	4331	2310

NAPHTHALENE—continued. 0.128 gram dissolved in 500 c.c.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to	3194	3130	3359	2976.5	3359	2976.5
" fairly strong to	3359	2976.5	—	—	—	—
" weak to	3439	2906.5	3439	2906.5	3439	2906.5
" feebly to	—	—	—	—	3561	2807
" very feebly to	—	—	3531	2831.5	—	—
Two feeble lines at	—	—	—	—	3647	2740
"	—	—	—	—	3701	2701
(4) Absorption band from	3439 to 4016	2906.5 to 2490.5	3531 to 3890	2831.5 to 2568	3701 to 3861	2701 to 2589
Rays transmitted very feebly at	4016	2490.5	3890	2568	—	—
And also at	4038	2476	—	—	—	—
Extending weakly and not continuously to ..	4331	2310	4331	2310	—	—
Rays transmitted at	—	—	—	—	3861	2589
" faint, not continuous to	—	—	—	—	4016	2490
" feeble continuous to	—	—	—	—	4374.4	2286
Thickness of layer of liquid.....	2 mm.		1 mm.			
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.		
Continuous, strong to	3359	2976.5	3359	2976.5		
" fairly strong to	3439	2906.5	3439	2906.5		
" weak to	3480	2875	3480	2875		
" faint to	—	—	3861	2589		
Weak, not continuous	3701	2701	—	—		
(4) Absorption band from	3701 to 3861	2701 to 2589	—	—		
Rays transmitted at	3861	2589	—	—		
Faint continuous spectrum to	4374.4	2286	4426.7	2259		

NAPHTHALENE—continued. 0.128 gram in 2500 c.c. of alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to	3359	2976.5	3359	2976.5	3493	2863
" fairly strong to	3439	2906.5	3439	2906.5	3647	2740
" weak to	3480	2875	3480	2875	4426.7	2259
" faint to	3611	2768	3890	2568	—	—
Feebly continuous to	3861	2589	—	—	—	—
Faint "	4426.7	2259	—	—	—	—
Continuous, weak to	—	—	4426.7	2259	—	—
Thickness of layer of liquid.....	2 mm.		1 mm.			
	Same as ..	the last.	—	—	—	—
Same as last with trace of a line at	—	—	4464.2	2240	—	—

NAPHTHALENE—continued. 0.128 gram in 12,500 c.c.

Thickness of layer of liquid.....		5 mm.		4 mm.		3 mm.	
Description of spectrum.		Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to		3493	2863	3493	2863	Same as last; a little stronger	
" fairly strong to		3647	2740	3890	2568		
" weak to.....		4426.7	2259	4426.7	2259		
Trace of a line at		4464.2	2240	—	—		
Feebly continuous to		—	—	4464.2	2240		
Two faint lines at		—	—	—	—		
Thickness of layer of liquid		2 mm.		1 mm.			
Continuous, strong to		Same as last.		3493	2863		
" fairly strong to				3890	2568		
" weak to.....				4426.7	2259		
Feebly continuous to				4474.2	2235		
Two faint lines at				4566.2	2190		
"				4660	2145.9		

ORTHO-XYLENE (Kahlbaum). 0.106 gram dissolved in 20 c.c. of alcohol.

Thickness of layer of liquid.....	25 mm.		20 mm.		15 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	3080	3245·5	3080	3245·5	3080	3245·5
" fairly strong to	3580	2793	3580	2793	3611	2768
" faint to	3611	2768	—	—	—	—
" weak to	—	—	3611	2768	—	—
Absorption band from	—	—	—	—	3611 to 4331	2768 to 2310
Rays transmitted feebly at	—	—	—	—	4331	2310
Thickness of layer of liquid	10 mm.		5 mm.		4 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	3080	3245·5	3080	3245·5	3080	3245·5
" fairly strong to	3611	2768	3647	2740	3647	2740
" feebly to	3647	2740	—	—	—	—
Absorption band from	3647 to 4331	2740 to 2310	3647 to 4331	2740 to 2310	3647 to 4331	2740 to 2310
Rays transmitted weakly at.....	4253	2352	4125	2424·3	—	—
Extend to	4378·2	2294	—	—	—	—
Continuously to.....	—	—	4426·7	2259	—	—
Rays transmitted at (just a trace)	—	—	—	—	4033	2479·5
Paint continuous from.....	—	—	—	—	4125	2424·3
To	—	—	—	—	4426·7	2259

ORTHO-XYLENE—*continued*. 0.106 gram dissolved in 20 c.c. of alcohol.

Thickness of layer of liquid.....	3 mm.		2 mm.		1 mm.	
	Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	3090	3245.5	3090	3245.5	3080	3245.5
" fairly strong to	3647	2740	3647	2740	3647	2740
" weak to	—	—	—	—	3677	2718
" very weak to	—	—	—	—	4426.7	2259
Absorption band from	3647 to 4331	2740 to 2310	3647 to 4331	2740 to 2310	—	—
Rays transmitted faintly at	4016	2490.5	—	—	—	—
Faintly, but not continuously to	4093	2444	—	—	—	—
Faint continuous spectrum to	4426.7	2259	—	—	—	—
Line faintly transmitted at	—	—	3707	2696.5	—	—
Rays transmitted at	—	—	4016	2490.5	—	—
Feebly continuous to	—	—	4426.7	2259	—	—

ORTHO-XYLENE—*continued*. 0.106 gram dissolved in 100 c.c. of alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	3090	3245.5	3080	3245.5	3080	3245.5
" fairly strong to	3647	2740	3677	2718	3707	2696.5
" weak to	4426.7	2259	—	—	—	—
" faint to	—	—	4464.2	2240	4464.2	2240
Thickness of layer of liquid.....	2 mm.		1 mm.			
Continuous, strong to	3080	3245.5	3090	3245.5	—	—
" fairly strong to	3707	2696.5	3707	2696.5	—	—
" faint to	4478	2233	4478	2233	—	—

ORTHO-XYLENE—continued. 0.106 gram dissolved in 500 c.c. of alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm. and 3 mm.		Wave-lengths. Oscillation frequencies.	Wave-lengths.
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.		
Continuous, strong to	3080	3245.5	3080	3245.5	—	—
" fairly strong to	3707	2696.5	3707	2696.5	—	—
" faint to	4478	2233	4478	2233	—	—
And to	—	—	4547.5	2199	—	—
Thickness of layer of liquid.....	2 mm and 1 mm.					
Continuous, strong to	3080	3245.5				
" fairly strong to	3707	2696.5				
" weak to	4426.7	2259				
" faint to	4566.2	2190				

METAXYLENE (Kahlbaum). 0.106 gram dissolved in 20 c.c. of alcohol.

Thickness of layer of liquid.....	25 mm		20 mm.		15 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to	3080	3245.5	Same as last.		3080	3245.5
" fairly strong to	3580	2793			3580	2793
" weak to	—	—			3611	2768

METAXYLENE—continued. 0.106 gram dissolved in 20 c.c. of alcohol

Thickness of layer of liquid	10 mm.		5 mm.		4 mm.	
	Oscillation frequencies	Wave-lengths	Oscillation frequencies	Wave-lengths	Oscillation frequencies	Wave-lengths
Continuous, strong to	3080	3245.5	3080	3245.5	3080	3245.5
• " fairly strong to	3580	2793	3611	2768	3647	2740
" weak to	3611	2768	—	—	—	—
" faint to	—	—	3647	2740	—	—
Absorption band from	3611 to 4331	2768 to 2310	3647 to 4331	2740 to 2310	3647 to 4331	2740 to 2310
Rays transmitted weakly at	—	—	4125	2424.3	4125	2424.3
Extension of spectrum to	—	—	4331	2310	4378.2	2284
Thickness of layer of liquid	3 mm.		2 mm.		1 mm.	
	Oscillation frequencies	Wave-lengths	Oscillation frequencies	Wave-lengths	Oscillation frequencies	Wave-lengths
Continuous, strong to	3080	3245.5	3080	3245.5	3080	3245.5
" fairly strong to	3647	2740	3647	2740	3647	2740
" very feebly continuous to	—	—	—	—	3890	2568
Absorption band from	3647 to 4331	2740 to 2310	3647 to 4331	2740 to 2310	—	—
Rays transmitted at	3701	2701	3701	2701	—	—
Continuous spectrum from	4125	2424.3	—	—	—	—
Extending faintly to	4378.2	2284	—	—	—	—
Also transmitted at	—	—	—	—	—	—
Faint not continuous to	—	—	3890	2568	—	—
Faint continuous to	—	—	4125	2424.3	—	—
Feebly continuous to	—	—	4378.2	2284	—	—
	—	—	—	—	4426.7	2259

METAXYLENE—continued. 0.106 gram dissolved in 100 c.c. of alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	3080	3245.5	3080	3245.5	The same as at 4 mm.	
" fairly strong to	3647	2740	3647	2740		
Very feebly continuous to	3890	2508	—	—		
Feebly continuous to.....	4426.7	2259	4426.7	2259		
Thickness of layer of liquid.....	2 mm.		1 mm.			
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths		
Continuous, strong to.....	3080	3245.5	3080	3245.5		
" fairly strong to.....	3647	2740	3647	2740		
" faint to.....	4426.7	2259	—	—		
" weak to.....	—	—	4464.2	2240		

METAXYLENE. 0.106 gram dissolved in 500 c.c.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	3080	3245.5	The same as at 5 mm.		The same as at 4 mm.	
" fairly strong to	3647	2740				
" weak to.....	4464.2	2240				

METAXYLENE—continued. 0.106 gram dissolved in 100 c.c. of alcohol.

Thickness of layer of liquid	2 mm.		1 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to	3080	3245.5	3080	3245.5
" fairly strong to	3647	2740	3647	2740
" weak to	4478	2233	4566.2	2190
Very feebly continuous to	4566.2	2190	—	—

PARAXYLENE (Kahlbaum). 0.106 gram dissolved in 20 c.c. of alcohol.

Thickness of layer of liquid	25 mm.		20 mm.		15 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to	3080	3245.5	3080	3245.5	3080	3245.5
" fairly strong to	3537	2826.5	3537	2926.5	3537	2826.5
" faint to	—	—	—	—	3580	2793

PARAXYLENE—continued. 0.106 gram dissolved in 20 c.c. of alcohol.

Thickness of layer of liquid.....	10 mm.		5 mm.		4 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to	3080	3245.5	3080	3245.5	3080	3245.5
" fairly strong to.....	3537	2926.5	3537	2926.5	3580	2793
" faint to.....	3580	2793	—	—	—	—
" weak to.....	—	—	3580	2793	—	—
" feebly to	3580 to 4331	2793 to 2310	—	—	3611	3768
(1) Absorption band from	4253	2352	3580 to 4331	2793 to 2310	3611 to 4331	2768 to 2310
Rays transmitted feebly at	4331	2310	—	—	—	—
Spectrum extends to	—	—	4125	2424.3	—	—
Rays transmitted at	—	—	4253	2352	—	—
Faint and not continuous to	—	—	4331	2310	—	—
Feebly continuous to.....	—	—	—	—	4125	2424.3
Rays transmitted weak at	—	—	—	—	4253	2352
And at.....	—	—	—	—	4347	2302.3
Faint spectrum at.....	—	—	—	—	4378.2	2284
Trace of a line at	—	—	—	—	—	—

Thickness of layer of liquid.....	3 mm.		2 mm.		1 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to	3080	3245.5	3080	3245.5	3080	3245.5
" fairly strong to	3580	2793	3580	2793	3611	2768
" weak to.....	3611	2768	3611	2768	—	—
(1) Absorption band from	3611 to 4331	2768 to 2310	3611 to 4331	2768 to 2310	3611 to 3701	2768 to 2701
Rays transmitted weakly at	4016	2490	4016	2490	—	—
Faint spectrum not continuous to	4136	2418	4136	2418	—	—
Single ray transmitted weakly at	—	—	—	—	3701	2701
(2) Absorption band from	—	—	—	—	3701 to 3890	2701 to 2568
Weak not continuous to	—	—	—	—	4016	2490.5
Faint continuous spectrum to	4378.2	2284	4378.2	2284	4378.2	2284

PARAXYLENE—continued. 0.106 gram dissolved in 100 c.c. of alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
• Description of spectrum.						
Continuous, strong to	3080	3245.5	3080	3245.5	3080	3245.5
" " fairly strong to	3611	2768	3611	2768	3611	2768
" " weak to	—	—	3635	2749	3635	2749
(1) Absorption band from	3611 to 3701	2768 to 2701	3635 to 3659	2749 to 2731	3635 to 3659	2749 to 2731
Single ray transmitted weakly at	3701	2701	—	—	—	—
A fairly strong line appears in the centre of this band at	—	—	3647	2740	—	—
Feebly continuous to	—	—	3701	2701	—	—
(2) Absorption band from	3701 to 3390	2701 to 2568	3701 to 3774	2701 to 2649.5	3701 to 3768	2701 to 2653
Rays transmitted faintly at	3797	2633.5	—	—	—	—
Weak discontinuous spectrum to	4016	2490.5	3900	2568	3900	2568
Faint continuous spectrum to	4378.2	2294	4378.2	2284	4426.7	2279
Fairly strong line at	—	—	—	—	3647	2740
Faint line at	—	—	4426.7	2259	—	—

PARAXYLENE—continued. 0.106 gram dissolved in 100 c.c. alcohol.

Thickness of layer of liquid	2 mm.		1 mm.	
	Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths.
Continuous, strong to	3080	3245.5	3080	3245.5
" fairly strong to	3611	2768	3611	2768
" weak to	3635	2749	3635	2749
" feebly to	—	—	4426.7	2259
(1) Absorption band from ..	3635 to 3659	2749 to 2731	—	—
Strong line at	3647	2740	—	—
Faint continuous to	3701	2701	—	—
(2) Absorption band from ..	3701 to 3768	2701 to 2653	—	—
Very feebly continuous to ..	3890	2568	—	—
Faint continuous to	4426.7	2259	—	—

PARAXYLENE—continued. 0.106 gram dissolved in 500 c.c. alcohol.

Thickness of layer of liquid	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths	The same as 5 mm., but stronger.		The same as 5 mm., but stronger.	
Continuous, strong to	3080	3245.5	The same as 5 mm., but stronger.		The same as 5 mm., but stronger.	
" fairly strong to	3611	2768				
" weak to	3635	2749				
" faint to	4426.7	2259	The same as 2 mm., with a faint line at 4566.2		The same as 2 mm., with a faint line at 2190	
Continuous, strong to	3808	3245				
" fairly strong to	8647	2740				
" weak to	4426.7	2259	The same as 2 mm., with a faint line at 2190		The same as 2 mm., with a faint line at 2190	
Faint line at	4464.2	2240				

PYRIDINE (Kahlbaum). 0.079 gram dissolved in 20 c.c. of alcohol.

Thickness of layer of liquid.....	5 mm., 4 mm., and 3 mm.	
Description of spectrum.	Oscillation frequencies.	Wave-lengths.
Weak continuous to	2259	4414
Strong "	2615	3825
Fairly strong continuous to.....	3493	2863
Weak continuous to	3586	2788
Feebly "	3611	2768
Thickness of layer of liquid	2 mm. and 1 mm.	
Weak continuous to	2259	4414
Strong "	2615	3825
Fairly strong continuous to.....	3493	2863
Weak continuous to	3647	2740

FARIDINE—continued. 0.079 gram dissolved in 100 c.c. of alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Weak continuous to	2259	4414	2259	4414	2259	4414
Strong "	3080	3245.5	3647	2740	3647	2740
Fairly strong continuous to	3647	2740	—	—	—	—
Very feebly "	3707	2696.5	—	—	—	—
Faint continuous to	—	—	3707	2696.5	—	—
Weak continuous to	—	—	—	—	3707	2696.5
Absorption band from	3707 to 4426.7	2696.5 to 2259	3707 to 4426.7	2696.5 to 2259	3707 to 4426.7	2696.5 to 2259
Rays transmitted very feebly at	4426.7	2259	—	—	—	—
Rays transmitted feebly from	—	—	4331	2310	—	—
To	—	—	4547.5	2199	—	—
Rays transmitted at	—	—	—	—	4316	2318
Spectrum extends, but is not continuous to	—	—	—	—	4566.2	2190
Thickness of layer of liquid	2 mm.		1 mm.			
	Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths.		
Weak continuous to	2259	4414	2259	4414		
Strong "	3647	2740	3647	2740		
Weak "	3707	2696.5	3707	2696.5		
Rays transmitted weakly to	—	—	3882	2609		
Absorption band from	3707 to 4426.7	2696.5 to 2259	3707 to 4253	2696.5 to 2352		
Rays transmitted at	4316	2318	4125	2424.3		
Not continuous to	4660	2148	—	—		
Faint, not continuous to	—	—	4301	2326		
Faint continuous to	—	—	4426.7	2259		
Spectrum extends, but is not continuous to	—	—	4660	2148		

PYRIDINE—continued. 0.079 gram dissolved in 500 c.c. of alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to	3647	2740	3647	2740	3647	2740
" fairly strong to	3707	2696.5	3707	2696.5	3707	2696.5
" weak to	3768	2653	3768	2653	3768	2653
" feeble to	—	—	3832	2609	3832	2609
Rays transmitted weakly to	3832	2609	—	—	—	—
Weak and not continuous to	—	—	—	—	3936	2538.5
Absorption band from	3768 to 4253	2653 to 2352	3768 to 4125	2653 to 2424.3	3768 to 4125	2653 to 2424.3
Rays transmitted at	4125	2424.3	4033	2479.5	4016	2490.5
Faint but not continuous spectrum at	4301	2326	4301	2326	4125	2326
" continuous to	4426.7	2259	4426.7	2259	—	—
Very feebly continuous to	—	—	4566.2	2190	4566.2	2190
Spectrum extends but is not continuous to	4680	2143	4680	2148	4680	2148
Thickness of layer of liquid.....						
2 mm. and 1 mm.						
Continuous, strong to	3647	2740	—	—	—	—
" fairly strong to	3707	2696.5	—	—	—	—
" weak to	3768	2653	—	—	—	—
" faint to	3890	2563	—	—	—	—
Very feebly continuous to	4301	2426	—	—	—	—
Weak continuous to	4426.7	2259	—	—	—	—
Very feeble continuous to	4566.2	2190	—	—	—	—
Spectrum not continuous, extends to	4680	2143	—	—	—	—

PRIDINE. 0.079 gram dissolved in 20 c.c. + HCl. 0.0365 gram in 20 c.c., or 0.1155 gram of the salt in 40 c.c.
Double thickness of cells taken.

Thickness of layer of liquid.....	10 mm.		8 mm.		6 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths.
Continuous, strong to	3080	3245.5			3090	3245.5
" fairly strong to	3531	2826.5			3531	2326.5
" weak to	3580	2793	The same as with 10 mm.		3611	2768
Faint to	3611	2768			—	—
Very feebly continuous to	—	—			3647	2740
Thickness of layer of liquid.....	4 mm.		2 mm.			
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths.
Continuous, strong to	3080	3245.5	3090	3245.5	—	—
" fairly strong to	3531	2826.5	3647	2740	—	—
" weak to	3647	2740	—	—	—	—
Absorption band from	3647 to 4426.7	2740 to 2259	3647 to 4426.7	2740 to 2259	—	—
Rays transmitted at one faint line	4426.7	2259	—	—	—	—
Rays transmitted weakly at	—	—	4331	2310	—	—
And extending, weak and not continuous to	—	—	4426.7	2259	—	—

Pyridine and HCl—continued. 0.1155 gram in 200 c.c., or equal to 0.1155 in 40 c.c. Diluted 2 c.c. to 10 c.c.

Thickness of layer of liquid.....	10 mm.		8 mm.		6 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to	3080	3245.5	3080	3244.5	3080	3245.5
" fairly strong to	3647	2740	3647	2740	3647	2740
Line at (just visible)	—	—	3701	2701	—	—
Very feebly continuous to	—	—	—	—	3701	2701
Absorption band from	3647 to 4426.7	2740 to 2259	3701 to 4331	2701 to 2310	3701 to 4316	2701 to 2318
Rays transmitted at	4331	2310	—	—	—	—
Extend weak, not continuous to	4426.7	2259	4426.7	2259	4426.7	2259
Thickness of layer of liquid.....	4 mm.		2 mm.			
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.		
Continuous, strong to	3080	3245.5	3080	3245.5		
" fairly strong to	3647	2740	3647	2740		
" faint to	3701	2701	3701	2701		
Very feebly continuous to	—	—	3762	2658		
Absorption band from	3701 to 4253	2701 to 2352	3762 to 4125	2658 to 2424.3		
Rays transmitted weak, but not continuous to ..	4566.2	2190	4253	2352		
Faint continuous to	—	—	4156.3	2244		
" not continuous to	—	—	4660	2145.9		

PYRIDINE and HCl—continued. 0.1155 gram dissolved in 1000 c.c.

Thickness of layer of liquid.....	10 mm.		8 mm.		6 mm.	
	Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	3080	3245.5	3080	3245.5	3080	3245.5
" fairly strong to.....	3647	2740	3647	2740	3647	2740
" weak to.....	3701	2701	3701	2701	3701	2701
Very feebly continuous to.....	3762	2658	—	—	—	—
Feebly continuous to.....	—	—	3762	2658	3762	2658
Absorption band from.....	3762 to 4125	2658 to 2424.3	3762 to 4125	2658 to 2424.3	3762 to 4028	2658 to 2482.5
Rays transmitted weak not continuous to.....	4253	2352	4253	2352	4253	2352
Weak continuous spectrum to.....	4456.3	2244	4426.7	2259	4426.7	2259
Not continuous to.....	4660	2145.9	4660	2145.9	4660	2145.9
Thickness of layer of liquid.....	4 mm.		2 mm.			
	Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths.		
Continuous, strong to.....	3080	3245.5	3080	3245.5		
" fairly strong to.....	3647	2740	3647	2740		
" weak to.....	3762	2658	3762	2658		
" faint to.....	—	—	4253	2352		
" weak to.....	—	—	4426.7	2259		
" faint to.....	—	—	4566.2	2190		
" feeble to.....	3890	2568	—	—		
Very feebly continuous to.....	4136	2418	—	—		
Faint continuous to.....	4253	2352	—	—		
Weak ".....	4426.7	2259	—	—		
Faint ".....	4460.3	2242	—	—		
" not continuous to.....	4660	2145.9	—	—		
Feebly continuous to.....	—	—	4660	3145.9		

DIPYRIDINE (Dr. Ramsay). 0.158 gram dissolved in 1000 c.c. alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to	3080	3245.5	3080	3245.5	3080	3245.5
" weak to	3392	2948	3392	2948	3392	2948
" faint to	3493	2863	3493	2863	3493	2863
Faint to	3580	2793	3580	2793	—	—
Lines fairly strong, but not continuous to.....	—	—	—	—	3580	2793
Fairly strong line at.....	—	—	—	—	3647	2740
Thickness of layer of liquid	2 mm.		1 mm.			
Continuous, strong to	3080	3245.5	3080	3245.5	—	—
" weak to	3392	2948	3392	2948	—	—
" faint to	3556	2812	3556	2812	—	—
Spectrum extends to.....	3890	2568	—	—	—	—
The lines are fairly strong, but not continuous to	—	—	3890	2568	—	—
Absorption band from	—	—	3890 to 4331	2568 to 2310	—	—
Rays transmitted from.....	—	—	4331	2310	—	—
To.....	—	—	4426.7	2259	—	—

DIPYRIDINE—continued. 0.158 gram dissolved in 5000 c.c. alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	3080	3245·5	3080	3245·5	3080	3245·5
" fairly strong to.....	—	—	3493	2863	3493	2863
" weak to.....	3392	2948	—	—	—	—
" faint to.....	3647	2740	3890	2568	3647	2740
The lines are fairly strong but not continuous to	3890	2568	—	—	—	—
Absorption band from.....	3890 to 4331	2568 to 2310	—	—	—	—
Rays transmitted from.....	4331	2310	—	—	—	—
To.....	4426·7	2259	—	—	—	—
Rays are transmitted very feebly to.....	—	—	4331	2310	—	—
Feebly continuous to.....	—	—	—	—	3890	2568
Rays transmitted feebly to.....	—	—	—	—	4331	2310
Spectrum extends to.....	—	—	4543·3	2201	4543·3	2201
Thickness of layer of liquid.....	2 mm.		1 mm.			
Continuous, strong to.....			3080	3245·5	—	—
" fairly strong to.....			3493	2863	—	—
" weak to.....			3647	2740	—	—
" faint to.....			4028	2482·5	—	—
Very feebly continuous to.....			4190	2387	—	—
Spectrum extends to.....			4660	2145·9	—	—

PICOLINE (Dr. Ramsay). 0.094 gram dissolved in 20 c.c. of alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	3080	3245.5	3080	3245.5	3080	3245.5
" weak to.....	3297	3033	3392	2948	3556	2812
" faint to.....	3392	2948	—	—	—	—
Faint to.....	3537	2826.5	—	—	—	—
Weak, not continuous to.....	—	—	3537	2826.5	—	—
Thickness of layer of liquid.....	2 mm.		1 mm.			
Continuous, strong to.....	3080	3245.5	3556	2812	—	—
" weak to.....	3556	2812	3580	2793	—	—
Fairly strong line at.....	3580	2793	—	—	—	—
Absorption band from.....	—	—	3580 to 4331	2793 to 2310	—	—

PICOLINE—*continued*. 0.094 gram dissolved in 100 c.c. alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	3556	2812	3580	2793	3580	2793
" weak to.....	3580	2793	—	—	—	—
Absorption band from.....	3580 to 4331	2793 to 2310	3580 to 4331	2793 to 2310	3580 to 4331	2793 to 2310
Rays transmitted at.....	—	—	4426.7	2259	4462.7	2259
Thickness of layer of liquid.....	2 mm.		1 mm.			
Continuous, strong to.....	3580	2793	3580	2793	—	—
" weak to.....	—	—	3611	2768	—	—
Absorption band from.....	3580 to 4331	2793 to 2310	3647 to 4331	2740 to 2310	—	—
Rays transmitted at.....	4426.7	2259	4426.7	2259	—	—

PICOLINE—continued. 0.094 gram dissolved in 500 c.c. alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	3580	2793	3580	2793	3580	2793
" weak to.....	3611	2768	3647	2740	3647	2740
Absorption band from.....	3647 to 4331	2740 to 2310	3647 to 4331	2740 to 2310	3647 to 4331	2740 to 2310
Rays transmitted from.....	4038	2476	4038	2476	3647	2740
To.....	4426.7	2259	4543.3	2201	3890	2568
Also from.....	—	—	—	—	4038	2476
To.....	—	—	—	—	4543.3	2201
Thickness of layer of liquid.....	2 mm.		1 mm.			
Continuous, strong to.....	3580	2793	3647	2740	—	—
" weak to.....	3647	2740	—	—	—	—
Absorption band from.....	3647 to 4331	2740 to 2310	—	—	—	—
Rays transmitted to.....	3980	2542	—	—	—	—
Also from.....	4016	2490.5	—	—	—	—
To.....	4543.3	2201	—	—	—	—
Feebly continuous to.....	—	—	4426.7	2259	—	—
Spectrum ends at.....	—	—	4560	2193	—	—

QUINOLINE. Specimen I. Prepared from Coal-tar. 0.129 gram dissolved in 20 c.c. of alcohol.

Description of spectrum.	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths.
Continuous, strong to	3080	3245.5	3080	3245.5	3080	3245.5
Thickness of layer of liquid.....	2 mm.		1 mm.			
Continuous, strong to	3080	3245.5	3080	3245.5	—	—
Feebly continuous to	—	—	3115	3208	—	—

QUINOLINE. Specimen I—continued. 0.129 gram dissolved in 100 c.c. of alcohol.

Description of spectrum.	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths.
Continuous, strong to	3080	3245.5	3080	3245.5	3080	3245.5
" faint to	3151	3171	—	—	—	—
" weak to	—	—	3151	3171	—	—
" fairly strong to	—	—	—	—	3151	3171
Thickness of layer of liquid.....	2 mm.		1 mm.			
Continuous, strong to	3151	3171	3151	3171	—	—

QUINOLINE. Specimen I—*continued*. 0.129 gram dissolved in 2500 c.c. of alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	3151	3171	3151	3171	3151	3171
" weak to.....	3647	2740	3647	2740	3890	2568
" faint to.....	4248	2355	4248	2355	4248	2355
Spectrum ends at	—	—	4296	2329	4326	2313
Thickness of layer of liquid.....	2 mm.		1 mm.			
Continuous, strong to.....	3151	3171	3647	2740	—	—
" fairly strong to	3647	2740	3890	2568	—	—
" weak to.....	3890	2568	4248	2355	—	—
" faint to.....	4326	2313	4331	2310	—	—
Two faint lines at	4371	2339	—	—	—	—
Spectrum extends to but is not continuous.....	4386.7	2264.5	4660	2148	—	—

QUINOLINE HYDROCHLORIDE. Specimen I—*continued*. 0.129 gram dissolved in 20 c.c. of alcohol. To the solution of Quinoline, HCl was added till the solution gave an acid reaction.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	2803	3569	2803	3569	2803	3569
" feebly to.....	—	—	2833.5	3530	—	—
" faint to.....	—	—	—	—	2833.5	3530
Very feeble line at	—	—	—	—	2887	3464

Thickness of layer of liquid	2 mm.		1 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	2803	3569	2803	3569
" weak to.....	2833.5	3530	2887	3464
" feeble to.....	2887	3464	—	—

QUINOLINE + HCl. Specimen I—continued. 0.129 gram dissolved in 100 c.c. of alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	2803	3569	2803	3569	2887	3464
" weak to.....	2887	3464	2887	3464	2918	3420
" feeble to.....	2918	3420	—	—	—	—
" faint to.....	—	—	2941	3403	2941	3403
Absorption band from	—	—	—	—	2941 to 3647	3403 to 2740

Thickness of layer of liquid.....	2 mm.		1 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	2887	3464	2887	3464
" weak to.....	2918	3420	2941	3403
" faint to.....	2941	3403	3008	3324
Absorption band from	2941 to 3647	3403 to 2740	3008 to 3647	3324 to 2740
Rays transmitted at	—	—	3525	2836.5
And extend, but are not continuous to	—	—	3890	2568
Line visible at	—	—	4044	2472.5

QUINOLINE + HCl. Specimen I—continued. 0.129 gram dissolved in 500 c.c. of alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	2887	3464	2887	3464	2887	3464
" weak to.....	2941	3403	3008	3324	3008	3324
" faint to.....	3008	3324	—	—	3073	3253
" feeble to.....	—	—	3073	3253	—	—
Absorption band from.....	3008 to 3647	3324 to 2740	3073 to 3647	3253 to 2740	3073 to 3647	3253 to 2740
Rays transmitted at.....	3325	2836.5	3493	2863	3493	2863
" extend (not continuous) to.....	—	—	4044	2472.5	—	—
" extend (feebly continuous) to.....	—	—	—	—	4044	2472.5
Thickness of layer of liquid.....	2 mm.		1 mm.			
	Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths.		
Continuous, strong to.....	2887	3464	3080	3245.5		
" weak to.....	3008	3324	—	—		
" faint to.....	3080	3245.5	—	—		
" feeble to.....	—	—	4130	2421		
Absorption band from.....	3080 to 3647	3245.5 to 2740	—	—		
Rays transmitted at.....	3487	2869	—	—		
" extend feebly continuous to.....	4014	2472.5	—	—		

QUINOLINE + HCl. Specimen I—continued. 0.129 gram dissolved in 2500 c.c. of alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	3080	3245.5	3080	3245.5	3080	3245.5
" feeble to.....	4136	2418	—	—	—	—
" faint to.....	—	—	3493	2863	3493	2863
" weak to.....	—	—	4044	2472.5	4044	2472.5
" faint to.....	—	—	4136	2418	4136	2418
Absorption band from.....	—	—	4136 to 4547.5	2418 to 2199	4136 to 4547.5	2418 to 2199
Rays transmitted at.....	—	—	—	—	4426.7	2259
Extend, but are not continuous to.....	—	—	—	—	4566.2	2190
Thickness of layer of liquid.....						
		2 mm.		1 mm.		
Continuous, strong to.....	3080	3245.5	The same as with 2 mm.			
" faint to.....	3359	2976.5				
" weak to.....	4044	2472.5				
" faint to.....	4136	2418				
Very feeble, not continuous to.....	4190	2387				
Absorption band from.....	4136 to 4547.5	2418 to 2199				
Rays transmitted at.....	4331	2310				
Extend to.....	4660	2148				

QUINOLINE. Specimen II. Prepared synthetically by Skraup's reaction. 0.129 gram dissolved in 20 c.c. of alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to	3080	3245.5	3080	3245.5	3080	3245.5
Thickness of layer of liquid.....	2 mm.		1 mm.			
Continuous, strong to.....	3080	3245.5	3080	3245.5	—	—

QUINOLINE. Specimen II—continued. 0.129 gram dissolved in 100 c.c. of alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	3080	3245.5	3080	3245.5	3080	3245.5
" faint to.....	—	—	3115	3208	3115	3208
Thickness of layer of liquid.....	2 mm.		1 mm.			
Continuous, strong to.....	3080	3245.5	3080	3245.5	—	—
" faint to.....	3151	3171	—	—	—	—
" weak to.....	—	—	3151	3171	—	—

QUINOLINE. Specimen II—continued. 0.129 gram dissolved in 500 c.c. of alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	3151	3171	3151	3171	3151	3171
" " feeble to.....	—	—	3359	2976.5	—	—
" " feeble to.....	—	—	—	—	3359	2976.5
Absorption band from.....	3151 to 3890	3171 to 2568	3359 to 3493	2976.5 to 2863	3359 to 3493	2976.5 to 2863
Rays transmitted feebly to.....	3890	2568	—	—	—	—
Rays transmitted to not continuous.....	—	—	4130	2421	—	—
" " weak at.....	—	—	—	—	3493	2863
Extend to but are not continuous at.....	—	—	—	—	4130	2421
Thickness of layer of liquid.....	2 mm.		1 mm.			
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.		
Continuous, strong to.....	3151	3171	3151	3171		
" " faint to.....	3359	2976.5	3647	2740		
" " feeble to.....	4130	2421	4185	2390		

QUINOLINE. Specimen II—continued. 0.129 gram dissolved in 2500 c.c. of alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	3151	3171	3151	3171	3151	3171
" fairly strong to.....	—	—	—	—	3647	2740
" weak to.....	—	—	3647	2740	4028	2482.5
" faint to.....	3647	2740	3890	2568	4190	2337
Spectrum extends to.....	—	—	—	—	4243	2358
Thickness of layer of liquid.....	2 mm.		1 mm.			
	Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths		
Continuous, strong to.....	3151	3171	3647	2740	—	—
" fairly strong to.....	3647	2740	3890	2568	—	—
" weak to.....	4028	2482.5	4186	2418	—	—
" faint to.....	4185	2390	4426.7	2259	—	—
Spectrum extends to (weak but not continuous).	4248	2355	4660	2145.9	—	—

PIPERIDINE (Kahlbaum). 0.085 gram dissolved in 20 c.c. of alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	3080	3245.5	3080	3245.5	3080	3245.5
" fairly strong to	3647	2740		2740	3647	2740
" weak to.....	3890	2568	3890	2568	3890	2568
" faint to	3970	2519	4016	2490.5	4016	2490.5
Weak line at	4038	2476	4038	2476	4044	2472.5
Spectrum extends feebly, but is not continuous to	—	—	4185	2390	4331	2310

Thickness of layer of liquid.....	2 mm.		1 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	3080	3245.5		
" fairly strong to	3647	2740	3647	2740
" weak to.....	3890	2568	3890	2568
" faint to	4044	2472.5	4130	2421
Very feebly continuous to.....	4185	2390	—	—
Spectrum extends to.....	4374.4	2286	—	—

TETRAHYDROQUINOLINE. A distillate boiling between 240° and 250° C. 0.133 gram dissolved in 20 c.c. of alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	3008.5	3324	3008.5	3324	3008.5	3324

TETRAHYDROQUINOLINE—continued. 0.133 gram dissolved in 20 c.c. of alcohol.

Thickness of layer of liquid.....	2 mm.		1 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	3008.5	3324	3073	3253
Fairly strong line at.....	3051.5	3275.5	—	—
Weak line at.....	3073	3253	—	—

TETRAHYDROQUINOLINE. A distillate boiling between 240° and 250° C. 0.133 gram dissolved in 100 c.c. of alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	3073	3253	3080	3245.5	3080	3245.5
Faint line at.....	—	—	—	—	3151	3171
Absorption band from.....	—	—	—	—	3151 to 3647	3171 to 2740
Very faint line at.....	—	—	—	—	3647	2740

Thickness of layer of liquid.....	2 mm.		1 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	3080	3245.5	3080	3245.5
" faint to.....	—	—	3151	3171
Fairly strong line at.....	3151	3171	—	—
Absorption band from.....	3151 to 3500	3171 to 2857.5	3151 to 3493	3171 to 2863
Rays transmitted faint, but not continuous to ..	3647	2740	—	—
Rays transmitted weak, but not continuous to..	—	—	3701	2701

TETRAHYDROQUINOLINE—*continued*. A distillate boiling between 240° and 250° C. 0.133 gram dissolved in 500 c.c. of alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	3080	3245·5	3080	3245·5	3080	3245
" weak to.....	3151	3171	3151	3171	3701	2701
Very feebly continuous to.....	3647	2740	3647	2740	—	—
Absorption band from.....	—	—	3701 to 4331	2701 to 2310	3768 to 4253	2653 to 2352
Rays transmitted, faint at	—	—	4331	2310	4426·7	2259
Thickness of layer of liquid.....	2 mm.		1 mm.			
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.		
Continuous, strong to.....	3080	3245·5	3080	3245·5		
" fairly strong to.....	3151	3171	3151	3171		
" weak to.....	3890	2568	3768	2653		
" very faint to	—	—	3890	2568		
Absorption band from	3890 to 4125	2568 to 2424·3	—	—		
Rays transmitted weak, but not continuous to..	4321	2315·5	—	—		
Very feebly continuous to	4426·7	2259	4253	2352		
Faint not continuous to	—	—	4426·7	2259		
Weak continuous to	—	—	4566·2	2190		
Spectrum extends very faint, not continuous to..	—	—	—	—		

TETRAHYDROQUINOLINE—*continued*. A distillate boiling between 240° and 250° C. 0.133 gram dissolved in 2500 c.c. of alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm. and 3 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	3080	3245·5	3080	3245·5
" fairly strong to.....	3151	3171	3151	3171
" weak to.....	3768	2653	3768	2653
" very faint to.....	3890	2568	—	—
" faint to.....	—	—	4253	2352
" weak to.....	—	—	4426·7	2259
Rays transmitted faint, but not continuous to ..	4253	2352	—	—
Weak continuous to ..	4426·7	2259	—	—
Spectrum extends very faint, but not continuous to ..	4543·3	2201	4566·2	2190
• Thickness of layer of liquid.....	2 mm.		1 mm.	
Continuous, strong to.....	The same as with 3 mm., but a little stronger.		3151	3171
Gradually weakening to.....			4566	2190

A portion of this substance with a different boiling point, from 235–240°, was dissolved in the same molecular proportion, i.e., 0.133 gram in 20 c.c. alcohol, and diluted accordingly. It gave identically the same photographs as the portion described here, which distilled over from 240–250°.

TETRAHYDROQUINOLINE HYDROCHLORIDE (Kahlbaum). 0.1695 gram dissolved in 20 c.c. of alcohol.

Thickness of layer of liquid.....	10 mm.		9 mm.		8 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	2615	3825	—	—	2615	3825
" weak to.....	2934	3411	—	—	3008	3324
" faint to.....	3008	3324	—	—	—	—
Faint line at	—	—	—	—	3073	3253
The same as with 10 mm., with a very feeble line at.....	—	—	3073	3253	—	—
Thickness of layer of liquid.....	7 mm.		6 mm.		5 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	—	—	2615	3825	2615	3825
" weak to.....	—	—	3008	3324	3008	3324
" faint to.....	—	—	3080	3245.5	3080	3245
Absorption band from	The same.	3080 to 3574	3080 to 3574	3245.5 to 2798	3080 to 3574	3245.5 to 2798
A single line transmitted at.....	—	—	3531	2831.5	—	—
{ With single lines transmitted at.....	—	—	—	—	3487	2869
	—	—	—	—	3531	2831.5
	—	—	—	—	3647	2740

TETRAHYDROQUINOLINE HYDROCHLORIDE—continued. 0.1695 gram dissolved in 20 c.c. of alcohol.

Thickness of layer of liquid.....	4 mm.		3 mm.		2 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	2615	3825	2615	3825	2615	3825
" fairly strong to.....	—	—	—	—	3008	3324
" weak to.....	3080	3245.5	3080	3245.5	3080	3245.5
" feeble to.....	—	—	—	—	3151	3171
Weak line at.....	—	—	3151	3171	—	—
Absorption band from.....	3080 to 3487	3245.5 to 2869	3151 to 3359	3171 to 2976.5	3151 to 3297	3171 to 3033
Rays transmitted at.....	3487	2869	3359	2976.5	3297	3033
To.....	3647	2740	—	—	—	—
Extend not continuous to.....	—	—	3647	2740	3647	2740
Thickness of layer of liquid.....	1 mm.					
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	2615	3825	—	—	—	—
" fairly strong to.....	3008	3324	—	—	—	—
" weak to.....	3080	3245.5	—	—	—	—
Feebly continuous to.....	3647	2740	—	—	—	—
Absorption band from.....	3647 to 4331	2740 to 2310	—	—	—	—

TETRAHYDROQUINOLINE HYDROCHLORIDE—continued. 0.1695 gram dissolved in 100 c.c. of alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	2615	3825	2615	3825	2615	3825
" fairly strong to	3008	3324	3008	3324	3080	3245.5
" weak to.....	3080	3245.5	3080	3245.5	3151	3171
" feeble to	3647	2740	3647	2740	3647	2740
• Absorption band from	3647 to 4331	2740 to 2310	3647 to 4331	2740 to 2310	3647 to 4331	2740 to 2310
Rays transmitted at	—	—	4331	2310	—	—
And extending (not continuous) to.....	—	—	4426.7	2259	—	—
Rays transmitted but not continuous from.....	—	—	—	—	3647	2740
To	—	—	—	—	3890	2568
Rays also transmitted at	—	—	—	—	4331	2310
Extend (not continuous) to.....	—	—	—	—	4426.7	2259
Thickness of layer of liquid.....	2 mm.		1 mm.			
	Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths.		
Continuous, strong to.....	2615	3825	2615	3825		
" fairly strong to	3080	3245.5	3080	3245.5		
" weak to.....	3187	3140	3187	3140		
" faint to.....	3647	2740	3647	2740		
Very feebly continuous to	—	—	3890	2568		
• Absorption band from	3647 to 4331	2740 to 2310	3647 to 4331	2740 to 2310		
Rays weakly transmitted from	3647	2740	4038	2476		
To	3890	2568	4426.7	2259		
Rays also transmitted at	4296	2339	—	—		
And extend (not continuous) to.....	4426.7	2259	—	—		

TETRAHYDROQUINOLINE HYDROCHLORIDE--continued. 0.1695 gram dissolved in 500 c.c. of alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	2615	3825			2615	3825
" fairly strong to	3080	3245.5			3080	3245.5
" weak to.....	3187	3140			3187	3140
" faint to	3647	2740	The same as 5 mm.		4426.7	2259
" very feeble to.....	3890	2568			—	—
Very feeble line at.....	—	—			4543.3	2201
Absorption band from	3647 to 4331	2740 to 2310			—	—
Reys transmitted at	4038	2476			—	—
Extend to	4426.7	2259			—	—
Thickness of layer of liquid.....	2 mm.		1 mm.			
The same, but a little stronger, and weak line at	The same	as 3 mm.	4555.8	2195	—	—

ORTHO-TOLUIDINE HYDROCHLORIDE. 0.107 gram of base dissolved in 20 c.c. of an alcoholic solution of hydrochloric acid.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	3080	3245.5			3493	2863
• " " strength	3359	2976.5	The same as 5 mm.		—	—
" " feebly to.....	3647	2740			—	—
Weak continuous to	—	—			3701	2701
Absorption band from	—	—			3701 to 4426.7	2701 to 2259
Rays transmitted very faint at	—	—			4426.7	2259
Thickness of layer of liquid.....	2 mm.		1 mm.			
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.		
Continuous, strong to	—	—	3647	2740	—	—
" " weak to	—	—	3701	2701	—	—
" " feebly to	—	—	3768	2653	—	—
Continuous to	3647	2740	—	—	—	—
Weak continuous to	3701	2701	—	—	—	—
Absorption band from	3701 to 4331	2701 to 2310	—	—	—	—
Rays transmitted feebly at	4125	2424.3	—	—	—	—
Spectrum extends to	4331	2310	4547.5	2199	—	—
Weak discontinuous to	4426.7	2259	—	—	—	—
Faint line at	4464.2	2240	—	—	—	—

PARATOLUIDINE. 0.107 gram dissolved in 20 c.c. of alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths	Oscillation frequencies.	Wave-lengths.
Continuous, strong to	3080	3245.5	3080	3245.5	3080	3245.5
" feeble to.....	—	—	3115	3208	—	—
" weak to.....	—	—	—	—	3115	3208
Feeble line at.....	—	—	3151	3171	—	—
Weak line at	—	—	—	—	3151	3171
Thickness of layer of liquid.....	2 mm.		1 mm.			
Continuous, strong to.....	3080	3245.5	3080	3245.5	—	—
" weak to.....	3115	3208	—	—	—	—
" fairly strong to	—	—	3151	3171	—	—
" very feeble to.....	—	—	3187	3140	—	—
Fairly strong line at	3151	3171	—	—	—	—

PARATOLUIDINE—continued. 0.107 gram dissolved in 100 c.c. of alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to	3080	3245.5	3080	3245.5	3080	3245.5
" fairly strong to	3151	3171	3151	3171	3151	3171
" very feeble to	3187	3140	—	—	—	—
" feeble to	—	—	3194	3130	—	—
Feebly continuous to	—	—	—	—	3194	3130
Absorption band from	3151 to 3701	3171 to 2701	3151 to 3647	3171 to 2740	3151 to 3647	3171 to 2740
Rays transmitted very faintly at	3701	2701	—	—	—	—
Rays transmitted at	—	—	3647	2740	3647	2740
And extends very weakly and not continuously to	—	—	3803	2629.5	—	—
Rays extend to	—	—	—	—	3832	2609
Thickness of layer of liquid.....	2 mm.		1 mm.			
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.		
Continuous, strong to	3080	3245.5	3080	3245.6		
" fairly strong to	3151	3171	3187	3140		
" weak to	3324	3008	3890	2568		
Absorption band from	3324 to 3493	3008 to 2863	—	—		
Rays transmitted at	3493	2863	—	—		
" extend weakly and not continuously to...	3890	2568	—	—		

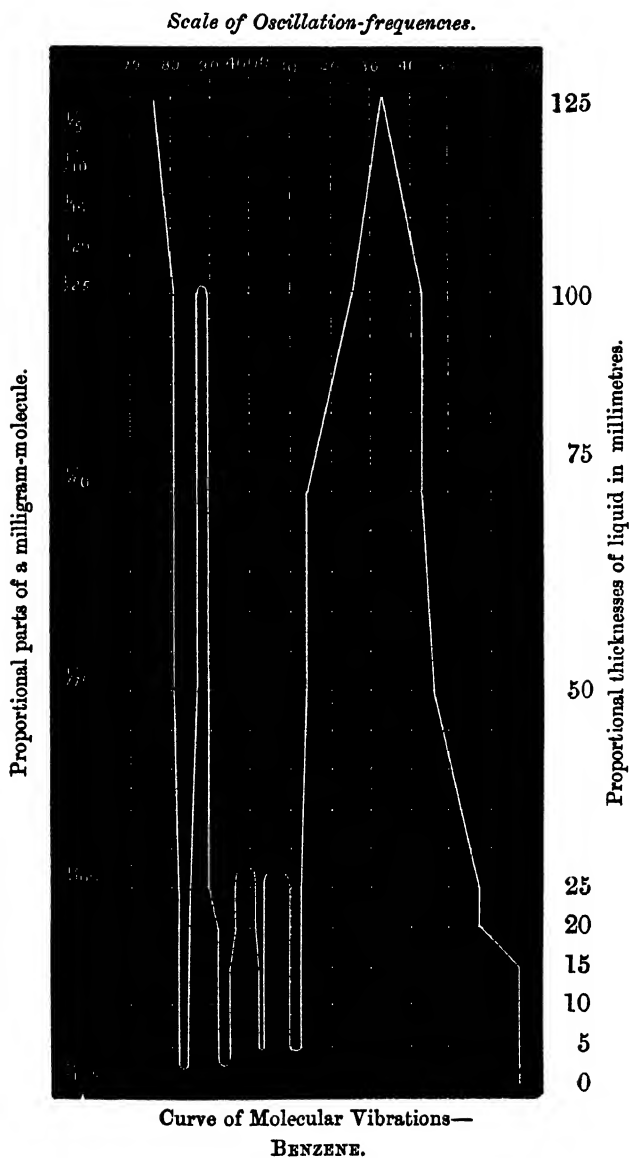
PARATOLUIDINE—continued. 0.107 gram dissolved in 500 c.c. of alcohol.

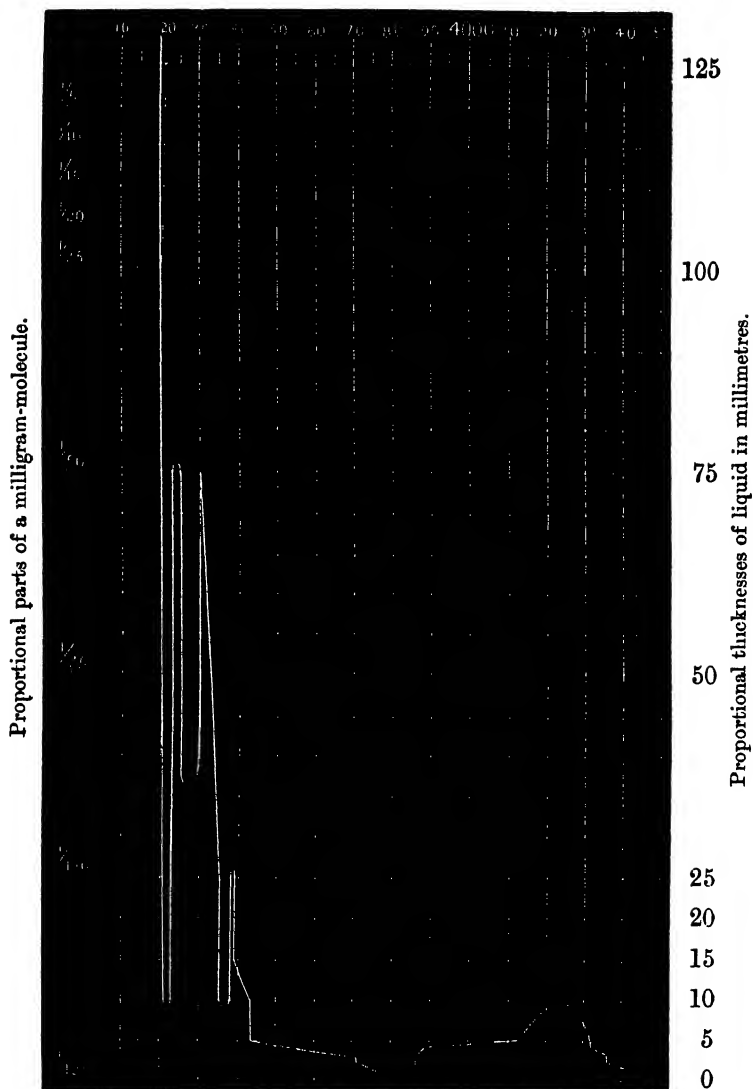
Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	3080	3245.5	The same as with 5 mm.		3080	3245
Fairly strong continuous to.....	3187	3140			3187	3140
Weakening progressively to.....	3930	2542			3930	2542
Thickness of layer of liquid.....	2 mm.		1 mm.			
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.		
Continuous, strong to.....	3080	3245.5	3080	3245.5		
Fairly strong continuous to.....	3187	3140	3187	3140		
The spectrum diminishing in strength to.....	4033	2479.5	4033	2479.5		
Absorption band from.....	3890 to 4426.7	2568 to 2259	4033 to 4331	2479.5 to 2310		
Rays transmitted very faint at.....	4426.7	2259	—	—		
Traces of lines at.....	4547.5	2199	—	—		
	4566.2	2190	—	—		
	4660	2145.9	—	—		
	—	—	4136	2418		
Rays transmitted, weak and not continuous, to.....	—	—	4660	2145.9		
Rays also transmitted weak, but not continuous to.....	—	—	—	—		

PARATOLUIDINE—continued. 0.107 gram dissolved in 2500 c.c. of alcohol.

Thickness of layer of liquid.....	5 mm.		4 mm.		3 mm.	
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	3080	3245	3187	3140		
" fairly strong to.....	3187	3140	—	—		
" weak to.....	—	—	4426.7	2259		
Spectrum diminishing in strength to.....	4033	2479.5	—	—		
Spectrum extends faintly to.....	—	—	4660	2145.9	The same as with 4 mm.	
Absorption band from.....	4033 to 4831	2479.5 to 2310	—	—		
Rays transmitted weakly at.....	4136	2418	—	—		
" also transmitted weakly, and not continuously to.....	4660	2145.9	—	—		
Thickness of layer of liquid.....	2 mm.		1 mm.			
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	The same as with 3 mm., but a little stronger.		3187	3140	—	—
Weakly continuous to.....			4660	2145.9	—	—

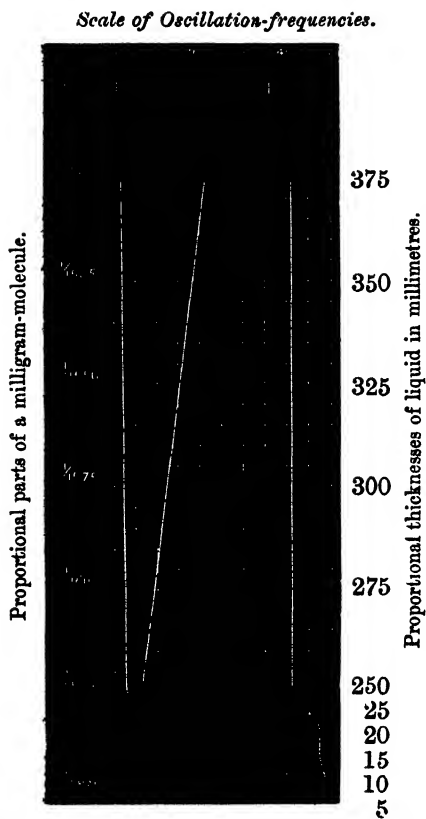
Thickness of layer of liquid.....	4 mm.		2 mm.			
	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.	Oscillation frequencies.	Wave-lengths.
Continuous, strong to.....	3080	3245·5	3080	3245·5	—	—
" fairly strong to.....	3701	2701	3701	2701	—	—
" feeble to.....	—	—	4566·2	2190	—	—
Decreasing in strength to.....	4547·5	2129	—	—	—	—



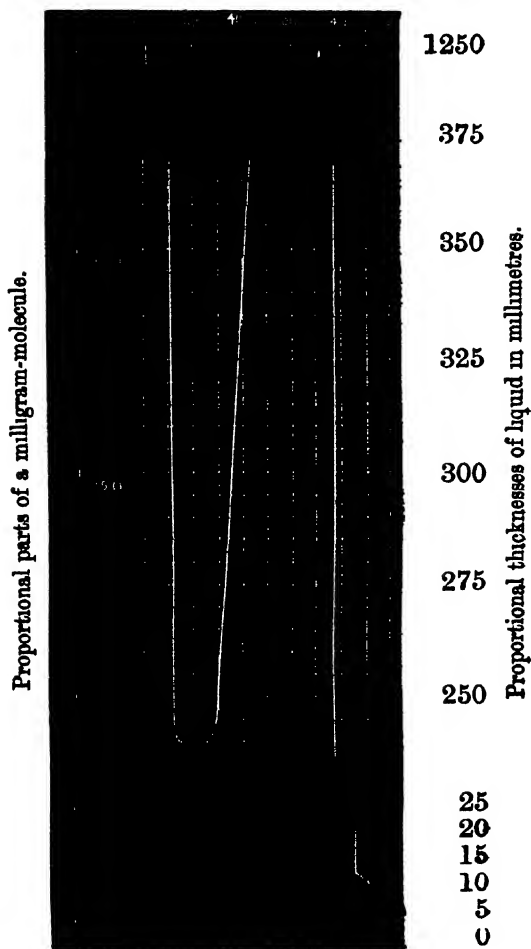
Scale of Oscillation-frequencies.

Curve of Molecular Vibrations—

NAPHTHALENE.

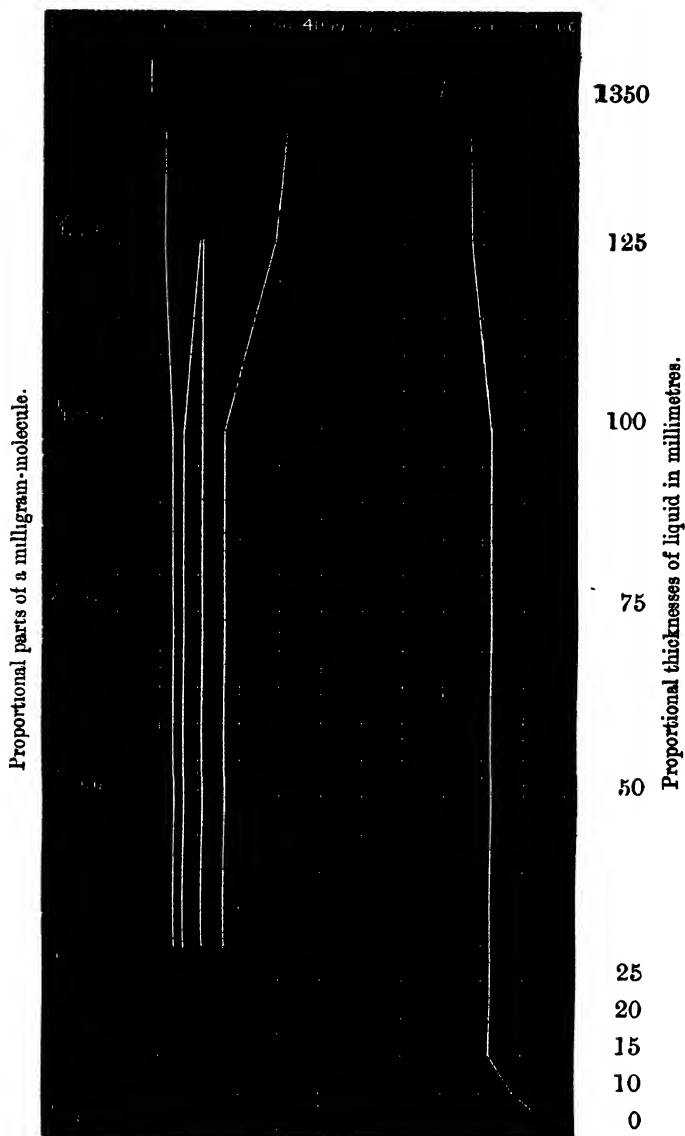


Curve of Molecular Vibrations—
ORTHXYLENE.

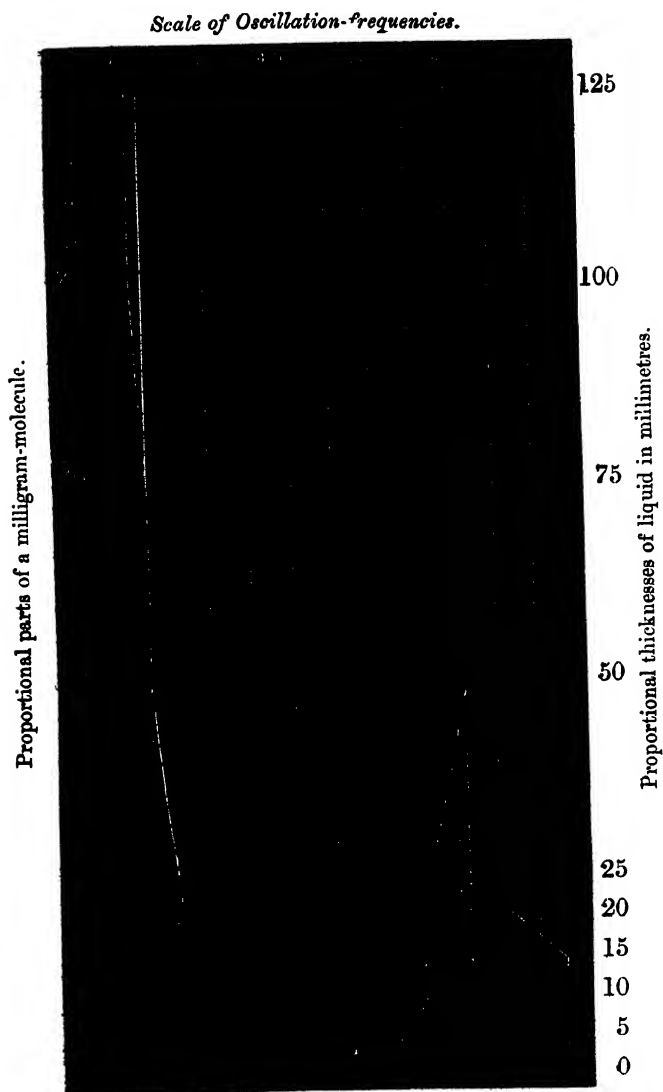
Scale of Oscillation-frequencies.

Curve of Molecular Vibrations—

METAXYLENE.

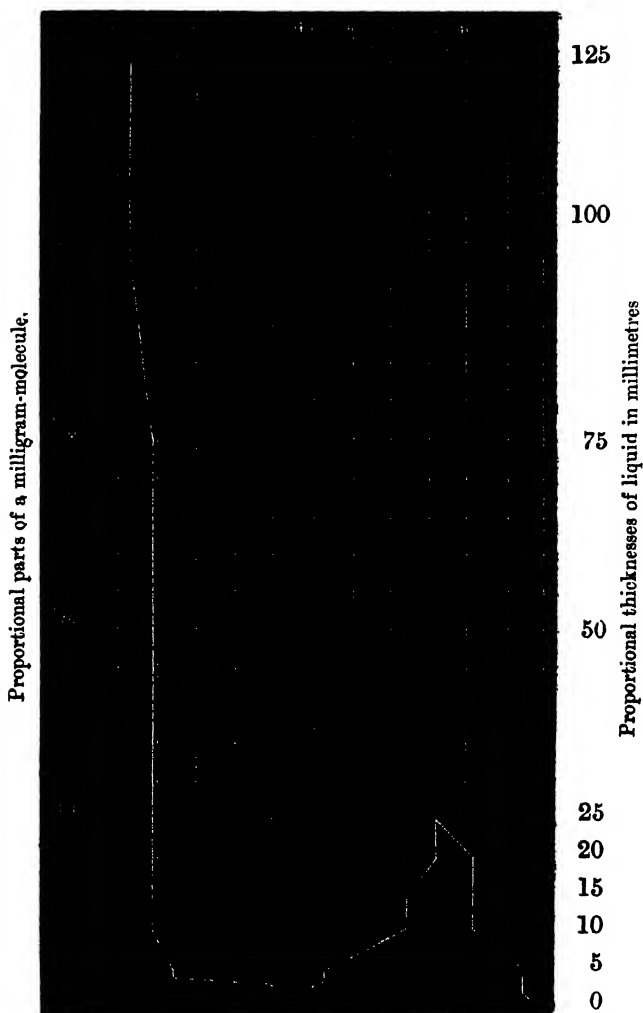
Scale of Oscillation-frequencies.

Curve of Molecular Vibrations—
PARAXYLENE.



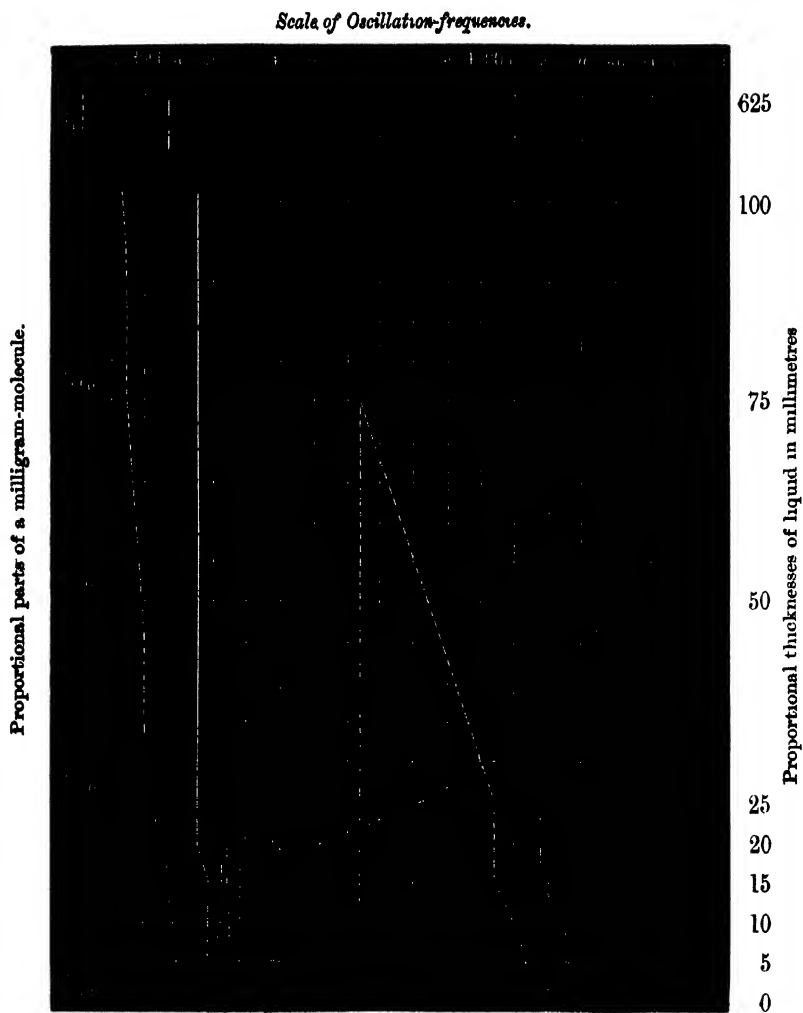
Curves of Molecular Vibrations—
PYRIDINE and PYRIDINE HYDROCHLORIDE.
The dotted line represents the hydrochloride.

Scale of Oscillation-frequencies.



Curve of Molecular Vibrations—

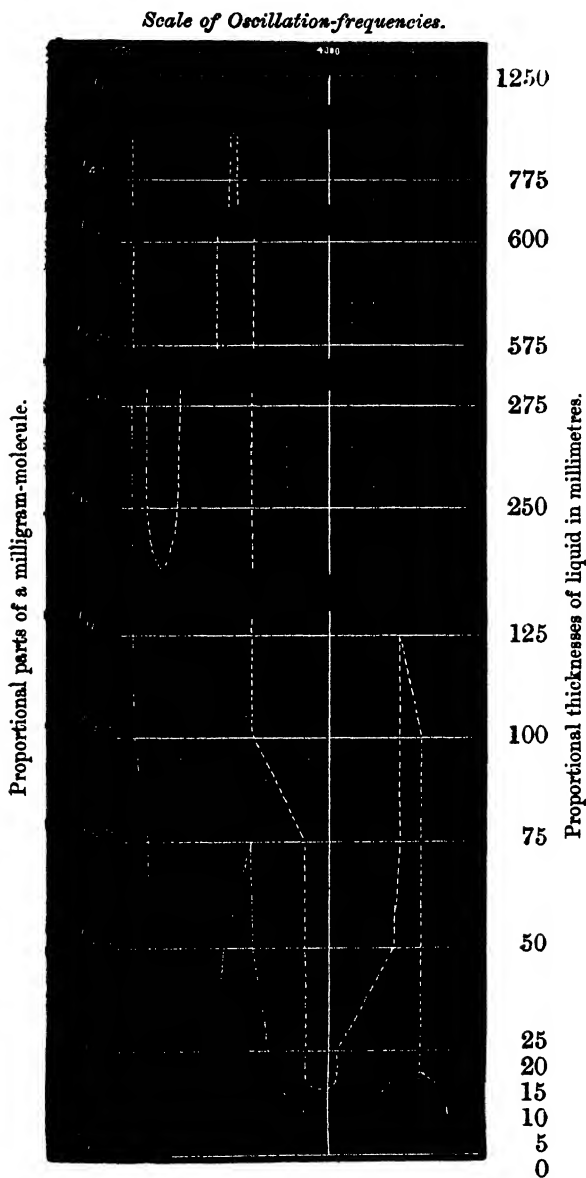
PICOLINE.



Curves of Molecular Vibrations—

QUINOLINE AND QUINOLINE HYDROCHLORIDE.

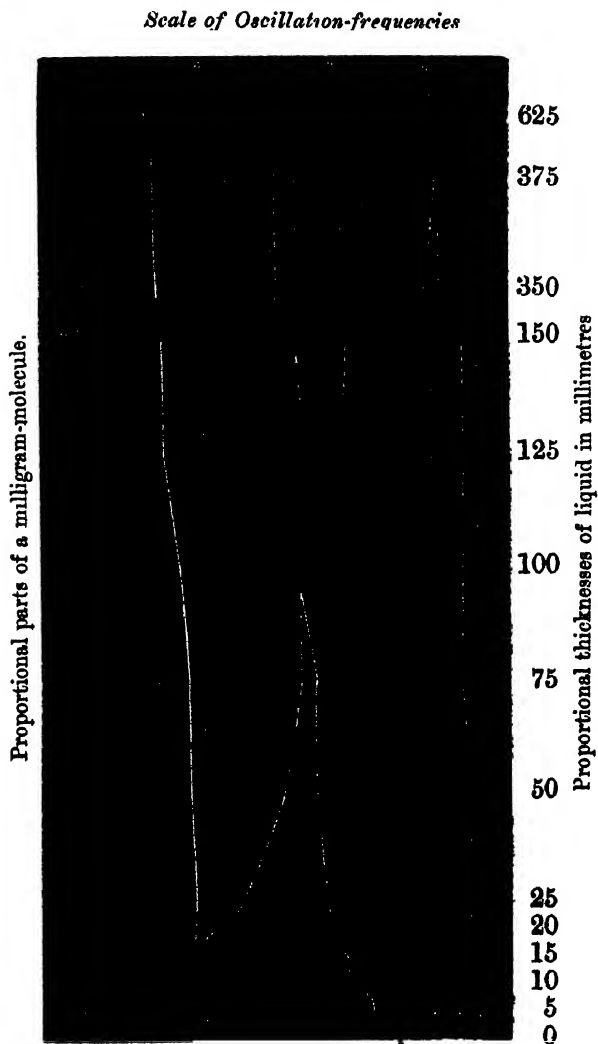
The dotted line represents the hydrochloride



Curves of Molecular Vibrations—

TETRAHYDROQUINOLINE and TETRAHYDROQUINOLINE HYDROCHLORIDE.

The dotted line represents the hydrochloride.

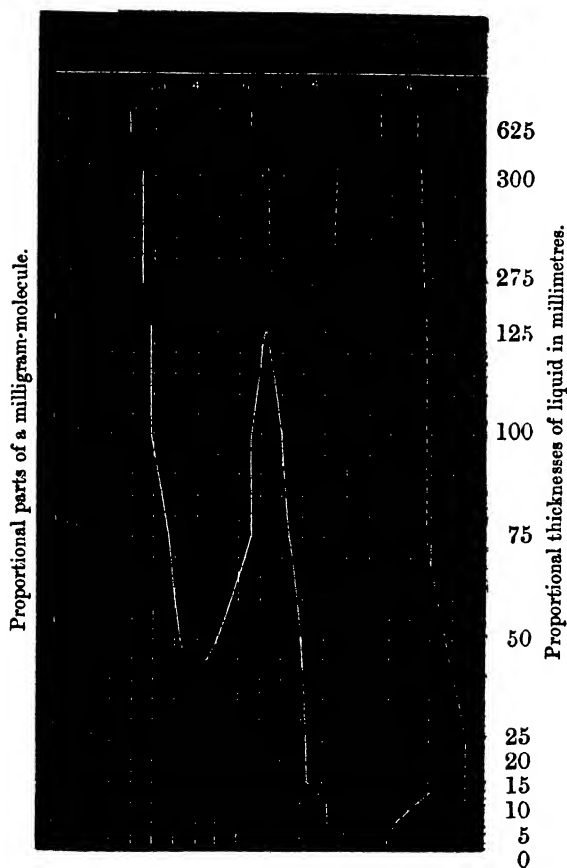


Curves of Molecular Vibrations—

ORTHOTOLUIDINE and ORTHOTOLUIDINE HYDROCHLORIDE.

The dotted line represents the hydrochloride.

Scale of Oscillation-frequencies.



Curves of Molecular Vibrations—

PARATOLUIDINE and PARATOLUIDINE HYDROCHLORIDE.

The dotted line represents the hydrochloride.

LXXIV.—*On the Action of Gypsum in Promoting Nitrification.*

By R. WARINGTON.

IN a communication recently made to the Chemical Society ("Nitrification, Part III," Trans., 1884, 637), I pointed out that the existence of more than a certain small proportion of soluble alkali in a solution entirely prevented nitrification from taking place. This prejudicial action of an excess of alkali was shown by disodium carbonate, by monosodium carbonate, and by ammonium carbonate, the quantity of disodium carbonate sufficient to prevent nitrification being smaller than that of the other carbonates named. Experiments were made in each case with a graduated series of solutions containing increasing quantities of soluble alkali. With monosodium carbonate as the alkali, nitrification was obtained, after many days, when the alkalinity equalled 350 parts of nitrogen as ammonia per million of solution; nitrification did not occur in the solutions of greater alkalinity. With ammonium carbonate as the alkali, nitrification took place after a considerable time when the alkalinity equalled 368 parts of nitrogen per million of solution; in the stronger solutions, nitrification did not take place. In a series of experiments with diluted urine of graduated concentration, nitrification was obtained after many days in a solution containing 12 per cent. of urine, the alkalinity of which (due to ammonium carbonate) at the commencement of nitrification was equivalent to 368 parts of nitrogen per million. Stronger solutions of urine did not nitrify.

All the solutions referred to above have been preserved up to the present time, but although the experiments have now continued considerably more than a year, nitrification has not occurred (with perhaps a single exception) in any solution of greater alkalinity than that named above. The possible exception is that of a 14 per cent. urine solution, belonging to the series above named. To the whole series of these solutions, 1 gram of soil was added on May 6, 1884. In the weaker solutions nitrification commenced in a few days. In the 10 per cent. solution, nitric acid was first found on July 7 (62 days). In the 12 per cent. solution, nitric acid appeared on August 4 (90 days). In the 14 per cent. solution, no nitrification had taken place on January 23, 1885 (262 days); nevertheless when examined in July, 1885, nitrification was found to be pretty far advanced. Of the alkalinity of this solution at the time when nitrification commenced, we have no knowledge, but in the previous September the alkalinity was equal to 412 parts of nitrogen per million. If we assume that the amount of ammonium carbonate found in

September continued unaltered at the commencement of nitrification, the limit of alkalinity already given (368 per million) will not be very seriously affected. In truth, however, the alkalinity of the solution must have been steadily diminishing, the diluted urine being kept in wide-mouthed loosely-stoppered bottles, less than half-filled ; opportunity was thus afforded for the access of air to the solutions, and for the gradual escape of the ammonium carbonate. It seems most probable, therefore, that the alkalinity of the solution slowly diminished, and that nitrification commenced when alkalinity had sunk to something like the point already mentioned. No nitrification has commenced in the 16 per cent. urine solution, although 16 months have elapsed since the experiment was started.

As the result of all the experiments, we may probably conclude that nitrification will not take place in solutions having an alkalinity of about 400 parts of nitrogen as ammonium carbonate per million of fluid ; whilst with an alkalinity of 368 parts per million nitrification may occur. An alkalinity somewhat above 400 per million does not, however, destroy the nitrifying organism, but merely suspends its action, as is shown by the last quoted experiment.

In the last communication to the Society, it was further shown that the degree of concentration of the solution had a considerable effect in retarding nitrification. This hindrance was, however, far less than that produced by the presence of soluble alkali. Thus while nitrification will not commence in the presence of 400 of nitrogen per million as ammonium carbonate, a solution containing more than 1000 per million of nitrogen as ammonium chloride has been completely nitrified, and nitrification is in progress in solutions of much greater concentration. In the case of solutions of ammonium chloride, a small amount of alkalinity was maintained by the presence of an excess of calcium carbonate.

From these results, it appeared highly probable that the limit of concentration (about 12 per cent.), beyond which urine ceased to be nitrifiable, might be greatly extended if measures were taken to prevent the production of a large quantity of ammonium carbonate in the early stages of the action. It was suggested in the last communication that this might be accomplished by the addition of gypsum to the urine ; the results of experiments in this direction will now be described.

On September 8, 1884, four urine solutions were prepared, containing respectively 15, 20, 30, and 50 per cent. of urine ; all of the solutions were thus above the strength previously found to be nitrifiable. 100 c.c. of each solution were placed in a short wide-mouthed bottle, similar to that used in the former experiments, and 22 mgrms. of precipitated gypsum added for each cubic centimetre of urine present ;

the quantity of gypsum was calculated from the amount of alkalinity shown by the fermented urine in the previous experiments. Each solution was finally seeded with 1 gram of soil. The solutions were agitated from time to time, to renew contact with the gypsum. The bottles were closed with cotton-wool.

As ammonium carbonate was developed in the solutions, the solid gypsum disappeared, and crystalline rounded masses (probably of calcium carbonate) were deposited on the sides of the bottles. As nitrification progressed these crystalline masses were again taken up by the liquid.

No nitrification was observed in any solution up to December 10, and fearing that the nitrifying organism might have been injured during the energetic changes which had taken place during the fermentation of the urine, a fresh seeding of soil was added on that date. The fear was probably groundless, for when next examined on January 23, 1885, nitrification was found to have made distinct progress in the 15, 20, and 30 per cent. urine solutions. The 50 per cent. solution showed no signs of nitrification on February 16, but on March 26 nitrification had distinctly commenced. The whole of the urine solutions treated with gypsum were thus found susceptible of nitrification.

Before the conclusion of the above experiments, and while it seemed doubtful whether the 50 per cent. urine solution would nitrify, a fresh series of trials was commenced. The solutions in this series contained respectively 15, 20, 30, 40, and 50 per cent. of urine; gypsum was added in the same proportion as before, but one solution containing 15 per cent. of urine was purposely left without gypsum. On February 7, 1885, a few particles of soil were added to each bottle, to set up the ammoniacal fermentation; when this stage was apparently completed, 1 gram of soil was added to each solution on March 13. The dates of the appearance of nitric or nitrous acid in each solution are given in the following table.

Commencement of Nitrification in Diluted Urine of various strengths, containing Gypsum, seeded with Surface Soil March 13th, 1885.

Urine in 100 of solution.	April 23, 41 days.	May 5, 53 days.	May 20, 68 days.	May 30, 78 days.	June 27, 106 days.	July 20, 129 days.	Aug. 11, 151 days.
15	none	distinct	—	—	—	—	—
20	"	none	distinct	—	—	—	—
30	"	"	trace	distinct	—	—	—
40	"	"	none	none	none	distinct	—
50	"	"	"	"	"	none	distinct

It will be noticed that nitrification occurred pretty soon in the case of the three weaker solutions, whilst an interval of 51 days elapsed between the nitrification of the 30 per cent. and 40 per cent. solutions. In the case of the 40 per cent. and of the 50 per cent. solutions, the sediment at the bottom of the bottle became for a time partially dark, and until this phase had passed over and the sediment resumed its normal colour no nitrification took place.

In this series of experiments, as in the former, the whole of the solutions treated with gypsum were found to be susceptible of nitrification. Nitrification commenced indeed in the stronger solutions only after a very considerable time, but a lengthening of the so-called period of incubation we have already learnt from numerous experiments always accompanies any increase in the concentration of the nitrifying fluid.

The 15 per cent. urine solution, which had not been treated with gypsum, but seeded equally with the others with 1 gram of soil, has remained unnitrified up to the present time.

The action of gypsum shown in these few experiments is quite in accordance with the observations of others. Thus Pichard (*Ann. agronom.*, 1884, 302), experimenting on the nitrification of earthnut-cake mixed with sand, found that by far the largest amount of nitric acid was produced when gypsum was added to the mixture; he supposes, however, that the sulphate of calcium had acted simply as an oxidising agent, and that its effect was due "à sa facilité d'être déoxydé au contact des matières organiques et réoxydé au contact de l'air." Joulie also, in his experiments on the loss of nitrogen during the fermentation of farmyard manure (*ibid.*, 289) found a formation of nitric acid only in those cases in which gypsum had been added to the mixture.

As the use of gypsum so greatly extends the limits of nitrification in the case of substances rich in ammonium carbonate, or other alkali, it seems probable that this property might be put to practical use if ever the artificial production of nitre were again to become remunerative, a state of things which must remain impossible while the present low price of sodium nitrate continues. Gypsum would probably be found a valuable ingredient of nitre-beds; it must also increase the oxidising power of the soil used in earth-closets. In cases also where strong sewage from factories or other large establishments is to be treated by application to land, the addition of gypsum would avoid the necessity of great dilution of the urine, and probably would enable oxidation to be effected by a smaller area of land.

In agriculture, the activity of dressings of farmyard manure would probably be increased by the addition of gypsum to the soil.

The experiments here described were carried out in the Rothamsted Laboratory.

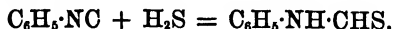
LXXV.—*Contributions toward the History of Formyl and Thioformyl Compounds derived from Aniline and Homologous Bases.*

By ALFRED SENIER, M.D.

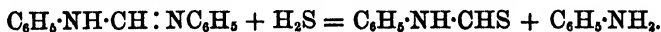
SOME years ago W. W. J. Nicol (*Ber.*, 15, 211) made the interesting observation that thioformanilide, when heated for some hours in a closed tube at 180°, is converted into a body having the composition of 2 mols. of the thioformanilide less 1 mol. of hydrogen sulphide. The nature of the substance thus produced is by no means fully made out. In the hope that the study of some homologous bodies might assist in elucidating this singular reaction, I have prepared the thioformyl derivatives of ortho- and para-toluidine as well as of the so-called pseudocumidine, which, by a recent development of tinctorial industry, has become available to the chemist. It must, however, at once be stated that difficulties far beyond what might have been expected were encountered in the preparation of these compounds, in consequence of which the main object of the experiments has, for a time at least, almost been lost sight of.

Preparation of Thioformyl-derivatives of Aniline and its Homologues.

The first of these thio-derivatives was discovered by A. W. Hofmann (*Ber.*, 10, 1095) as the result of the action of hydrogen sulphide on phenyl isocyanide:—



In this manner he obtained thioformanilide. Bernthsen (*Annalen*, 192, 35) somewhat later prepared the same compound by passing dry hydrogen sulphide through melted methenyldiphenylamidine, when aniline is formed and can be pretty easily separated:—

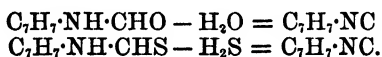


Lastly, Hofmann (*Ber.*, 11, 338) has recommended a readier method, which consists in submitting the formyl-derivative of the aromatic monamine to the action of phosphorus pentasulphide, when the sulphur of the pentasulphide exchanges place with the oxygen of the formyl-group.

The last method has given me the thioformyl-derivatives of ortho-toluidine, paratoluidine, and also of the so-called pseudocumidine. The reaction is, however, far more complex with the homologues of aniline than with aniline itself, although even this, according to Hofmann's statement, does not furnish more than 60 per cent. of the

theoretical yield, and then only when small quantities are operated on. In the case of the toluidines, the reaction by no means consists exclusively in the exchange of oxygen for sulphur. Other changes invariably take place, giving rise to the formation in each instance of amidines, together with compounds of an indeterminate nature. The amidine is obviously the result of the action of heat on the thio-compound; for when these compounds are strongly heated, they readily yield the corresponding amidine; moreover, the gases evolved in the reaction are unmistakably the same as those which are given when the pure thio-derivative is converted into amidine by heat. Indeed, treatment of formyl compounds with phosphorus pentasulphide may be employed for the preparation of formylic amidines.

Amongst the other products of the reaction was a remarkable crystalline phosphorus compound obtained only in very small quantity. Isocyanamide is also always formed to a small extent, which is not surprising if its close relation to the formyl and thioformyl compounds be remembered:—



The difficulties encountered more especially in the preparation of thioformoparatoluidide were so great that the Bernthsen process and even Hofmann's original method were tried. The compound was indeed obtained by each of these processes, but, on the whole, treatment of the formyl body with phosphorus pentasulphide is to be preferred.

Thioformorthotoluidide.

Formorthotoluidide was prepared by distilling a mixture of formic acid and orthotoluidine in theoretically equivalent proportions. Throughout the operation there was a slight odour of the isocyanide. The product obtained, after redistillation and rejection of the first and last portions, gave 65 per cent. of the theoretical yield. Form-orthotoluidide thus obtained had the properties ascribed to it by Ladenburg (*Ber.*, 10, 1129). It forms a *sodium-derivative*, which may be purified by recrystallisation from alcohol. This compound, however, does not form quite so readily as in the case of the para-compound to be mentioned later.

To obtain the thio-derivative, the formyl compound and phosphorus pentasulphide, both in powder, were mixed in the proportions employed by Hofmann in the corresponding aniline reaction—5 parts of the former to 3 of the latter; this mixture was then heated by means of a paraffin-bath, care being taken to keep it well stirred. The heating was continued till the substance, having melted, a

decided effervescence began, and the surrounding atmosphere was permeated with an intensely and persistently bitter taste. At this point, the thermometer immersed in the mixture indicated 120° . The best yield is obtained by stopping the reaction at this stage; for, if the temperature is allowed to rise, large quantities of the thio-compound are converted into amidine, or indeed it may happen that all the thio-compound undergoes this transformation. The gas which escaped, besides the bitter taste due undoubtedly to suspended particles of the thio-compound, consisted apparently for the most part of carbon bisulphide and hydrogen sulphide. The product, when cool, was powdered and extracted with cold dilute sodium hydroxide solution, which dissolves the thio-derivative, as might have been expected from the behaviour of the corresponding aniline compound. Addition of hydrochloric acid to this solution yielded the crude thio-compound which had still to be purified by two or three crystallisations from alcohol. The yield obtained was 13–14 per cent. of that obtainable were the reaction a simple exchange of oxygen for sulphur.

The substance exhibited a constant melting point of $94\text{--}96^{\circ}$. Elementary analysis led to the formula $\text{C}_8\text{H}_7\cdot\text{NH}\cdot\text{CHS} = \text{C}_8\text{H}_7\text{NS}$, which requires the following values:—

	Theory.		Experiment.	
C_8	96	63.58	63.15	—
H_7	9	5.96	6.38	—
N	14	9.27	—	—
S	32	21.19	—	21.66
	<hr/>	<hr/>		
	151	100.00		

Thioformorthotoluidide crystallises from alcohol in yellow needles, having a persistent and intensely bitter taste. It is insoluble in water, but soluble in alcohol and ether. Concentrated soda solution converts it into toluidine and formate, especially on heating. In cold dilute soda solution, it dissolves without being appreciably acted on, and from this solution, as has been pointed out, it is reprecipitated on the addition of an acid. Heated in a closed tube, 2 mols. lose 1 mol. of hydrogen sulphide, forming a compound to be presently described.

By distillation in a vacuum, thioformorthotoluidide gives *methenyl-diorthotolylamidine*, with an escape of gases containing hydrogen sulphide and carbon bisulphide, the latter recognised by its action on triethylphosphine. This amidine was purified and analysed. It melted constantly at 151° , whilst the melting point observed by Ladenburg

(*Ber.*, 10, 1260), who first described it, was 150—153°. Analysis led to the formula $\text{HC} \begin{smallmatrix} \text{NC}_7\text{H}_7(o) \\ \text{NHC}_7\text{H}_7(o) \end{smallmatrix} = \text{C}_{18}\text{H}_{18}\text{N}_2$, which requires—

	Theory.		Experiment.	
C ₁₈	180	80·36	80·69	—
H ₁₈	16	7·14	7·41	—
N ₂	28	12·50	—	12·43
	<hr/>	<hr/>		
	224	100·00		

The residue from which cold dilute soda solution had extracted the thio-compound, gave to hot alcohol an abundant yield of the substance just described, having the same melting point and giving the general reaction for amidines—a hydrochloride soluble in water, but precipitated on the addition of concentrated hydrochloric acid.

Thioformoparatoluidide.

Formoparatoluidide was prepared from paratoluidine in the same manner as formorthotoluidide from orthotoluidine. It was purified by redistillation and by conversion into a beautiful crystalline *sodium-derivative*, which, from its analogy to the corresponding aniline compound, has doubtless the formula $\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{CNaO}$. The pure formoparatoluidide thus obtained melted constantly at 52—53°, and, submitted to ultimate analysis, it gave the formula $\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{CHO} = \text{C}_8\text{H}_9\text{NO}$. This requires—

	Theory.		Experiment.	
C ₈	96	71·11	71·62	—
H ₉	9	6·67	6·86	—
N	14	10·37	—	10·57
O	16	11·85	—	—
	<hr/>	<hr/>		
	135	100·00		

These numbers and melting point agree with those obtained by Tobias (*Ber.*, 15, 2446), whom I subsequently ascertained had already prepared this compound, but who does not appear to have observed the sodium salt. The yield obtained was 60 per cent. of that calculated for a complete reaction.

Formoparatoluidide was treated with phosphorus pentasulphide precisely in the same manner as formorthotoluidide. The temperature at which distinct effervescence commenced was some 10° higher than in the case of the ortho-compound. It was found exceedingly difficult to adjust the temperature so as to prevent the action going too far

and thus to avoid the whole of the thio-derivative being converted into the amidine. Much more amidine than thio-compound was always obtained; in the most favourable experiments, the yield did not amount to more than 3 or 4 per cent. of that which would be obtained were the reaction a simple one. The best way of proceeding was found to be to divide the mixture of formoparatoluidide and phosphorus pentasulphide between a number of test-tubes and heat each separately, when an average yield was obtained better than what generally resulted from operating with larger quantities, where it was much more difficult to regulate the temperature.

After two or three crystallisations from alcohol, the substance melted constantly at 173.5° , and was found on elementary analysis to have the formula $C_7H_7 \cdot NH \cdot CHS = C_6H_5NS$, requiring the numbers—

	Theory.		Experiment.	
C ₆	96	63.58	63.93	—
H ₇	9	5.96	6.43	—
N	14	9.27	—	—
S	32	21.19	—	21.25
	<hr/>	<hr/>		
	151	100.00		

Thioformoparatoluidide when crystallised from alcohol forms yellow needles, insoluble in water, soluble in alcohol and ether, and having the same bitter taste as the corresponding aniline and orthotoluidine derivatives. Like the latter, it is soluble in cold dilute soda solution, and is reprecipitated therefrom by acids. Hot concentrated soda solution decomposes it into toluidine and formate. Heated in a closed tube for seven hours at 190° , it evolves hydrogen sulphide, and forms an oil with little or no crystalline compound, quite different from what is observed in the case of the aniline and orthotoluidine compounds.

Distilled in a vacuum, thioformoparatoluidide is decomposed in the same manner as the aniline and orthotoluidine derivatives, giving a distillate of crystalline *methenyldiparatolylamidine*. This substance is also extracted by alcohol from the residue insoluble in cold dilute soda solution obtained in the above reaction, and will be described presently. If prior to treating this residue with hot alcohol it be subjected to the action of boiling water, there will generally be found to separate from the water on cooling a small quantity of beautiful yellow needles of a *phosphorus compound*. Enough of this body was not obtained to admit of purification. It melted at about 250° , and gave on analysis C 56.47 per cent., H 6.95 per cent. Besides carbon, hydrogen, and phosphorus, it contained nitrogen, but no sulphur. If further

examined it may possibly prove to be a body analogous to those obtained by Jackson and Menke (*Amer. Chem. J.*, 1882-3, 380) when submitting aniline to the action of phosphorus chloride.

Thioformoparatoluidide was also prepared by Bernthsen's method and by Hofmann's original plan, but these processes do not offer advantages which recommend them in place of the one employed.

Methenyldiparatolylamidine.

It has already been shown that where phosphorous pentasulphide is allowed to act upon formortho- or formopara-toluidide, the corresponding amidines are formed, especially when a high temperature is employed. By this method, too, formanilide yields *methenyldiphenylamidine*, the yield obtained being about 25 per cent. It has also been shown that by distilling thioformorthotoluidide or thioformoparatoluidide in a vacuum the corresponding amidine distils over; this too is the case with thioformanilide. It is also probable, in view of some unfinished experiments, that the same reactions occur with pseudocumidine.

Of these amidines, the only new one analysed is *methenyldiparatolylamidine*. It was obtained from the residue insoluble in cold dilute soda solution in the preparation of thioformoparatoluidide by treatment with hot alcohol. After successive recrystallisations, it gave a constant melting point of 141°. It very readily forms a beautiful crystalline *platinochloride*, in which the platinum was determined, showing the formula to be $\left[\text{HC} \begin{smallmatrix} \text{NC}_7\text{H}_7(p) \\ \text{NHC}_7\text{H}_7(p) \end{smallmatrix} \right]_2\text{PtCl}_6$, which requires—

Theory.	Experiment.
22.95	22.69

Methenyldiparatolylamidine is insoluble in water but soluble in alcohol and ether. It crystallises easily from a mixture of alcohol and water in well-formed short rhombic prisms and plates, and gives a hydrochloride soluble in water but insoluble in concentrated hydrochloric acid.

The same reactions and the same melting point were observed in the case of the amidine obtained by distilling thioformoparatoluidide in a vacuum.

Formocumidine.

Cumidine and formic acid mixed in equivalent proportions were distilled twice, and the solidified distillate dissolved in alcohol, and several times recrystallised therefrom until the melting point was

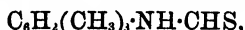
constant at 121°. The analysis corresponded with the following formula: $C_6H_2(CH_3)_3 \cdot NH \cdot CHO = C_{10}H_{13}NO$, and this requires—

	Theory.		Experiment.
C ₁₀	120	73·62	73·67
H ₁₃	13	7·98	8·33
N	14	8·59	—
O	16	9·81	—
	163	100·00	

Formocumidide crystallises in colourless needles, sparingly soluble in water, but soluble in alcohol and ether.

Thioformocumidide.

Formocumidide was mixed with phosphorus pentasulphide and treated as previously described in the case of the corresponding compounds of toluidine. A crystalline substance was produced, doubtless *methenyldicumylamidine*, which alcohol extracted from the residue undissolved by the soda solution, and a well-formed crystalline body, having all the characters which *thioformocumidide*,



may be expected to possess. Unfortunately the quantity of the compound at my disposal was not sufficient to enable me to free it from some bye-product rich in sulphur. Thus the sulphur determinations could not be brought below 19·9 per cent., whereas the cumidide in question requires only 17·88 per cent. This substance gives off hydrogen sulphide when heated, and if distilled in a vacuum no doubt would give the amidine.

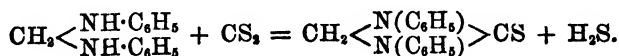
Action of Heat in Closed Tubes on Thioformanilide and its Homologues.

It has already been stated that owing to the difficulty experienced in preparing sufficient quantity of the thioformyl bodies, the original object of the inquiry has as yet scarcely been broached. Still I should not leave unmentioned that I have repeated Nicol's experiment, obtaining, as might have been expected, results identical with those described by him. Experiments made with the thioformyl-derivatives of ortho- and para-toluidine and cumidine have proved that these compounds exhibit an analogous behaviour. As yet, however, I have only been able to study somewhat more in detail the compound obtained from the thioformyl-derivative of orthotoluidine.

The tube containing the substance was heated for some hours at 190°. On opening it, there was an abundant escape of hydrogen sulphide, while a substance partly oily and partly crystalline remained in the tube. The oil was removed by a small quantity of alcohol, and the crystals thus obtained, after being recrystallised several times from alcohol, exhibited a constant melting point of 160°. They consisted of yellow needles, insoluble in water, but soluble in alcohol and ether, and, like the corresponding aniline compound, have no bitter taste. On analysis, they were found to yield 12·32 per cent. of sulphur. The compound consequently is homologous with the compound discovered by Nicol, and consists of 2 mols. of thioformorthotoluidide less 1 mol. of hydrogen sulphide: $2C_7H_7 \cdot NH \cdot CHS - H_2S = C_{16}H_{16}N_2S$, which contains 11·94 per cent. of sulphur.

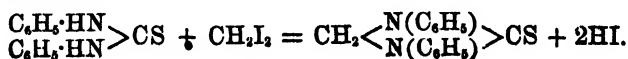
When thioformoparatoluidide is heated in the same manner, it gives only an oil. It is to be noted that an oily substance is produced in the reaction with the aniline compound, and to a greater extent in that of thioformorthotoluidide, whilst in the case of the para-derivative it seems to be exceedingly difficult at least to avoid the whole product being oily. The oil in the latter case gave no indication of combination with acids or alkalis, and when steam was passed through it did not distil, but separated into two parts, the smaller part crystalline and heavier, and the larger part oily and lighter than water.

Two attempts were made to prepare these condensed thio-compounds by an altogether different method, and thus to throw light on their constitution. Both these series of experiments, although they led to results interesting in themselves, furnished no information of a character to aid the object in view. The methylenediphenyldiamine of Madame Lermontoff (*Ber.*, 7, 1255) was prepared, and this was acted on by carbon bisulphide, when it was hoped that the following reaction would take place, giving at least an isomeride of the desired body:—



Hydrogen sulphide escaped in abundance, and a base remained distinctly different from the original substance, but not possessing the characters of the condensed thio-compound obtained by Nicol.

In the second place, thiocarbamilide was treated with methylene iodide in a closed tube at 100°. The following reaction would have given a compound also of the same empirical formula as the desired thio-derivative:—



Such compounds have been previously obtained in a somewhat similar way in the case of ethylene by W. Will (*Ber.*, **14**, 4485). From the contents of the tube, a beautiful white crystalline compound was extracted, which although not thiocarbanilide, was quite different in its properties from the thio-derivative sought.

Thus although on the whole but little additional information has been gained by this inquiry respecting the reaction which formed its object, still a number of interesting reactions have been brought to light, many of them indicating paths for future work.

Action of Phenyl Isocyanate on Formyl- and Thioformyl-derivatives of Aniline and its Homologues.

In conclusion, a series of beautiful crystalline compounds may be mentioned, which result from the action of phenyl isocyanate on formyl- and thioformyl-derivatives of aniline and ortho- and para-toluidine. The isocyanate may be simply added and allowed to stand with an ethereal solution of the formyl- or thioformyl-derivative, when the new compound comes out in splendid crystals; but it is better to heat the two substances together in a closed tube at 100° for a few hours. In either case, the crude product is freed from excess of isocyanate by washing with ether, in which the new compound is insoluble, and it is then purified by recrystallisation from alcohol. Care must be taken that no water is present, as this would produce carbanilide. Although, as yet, these substances have not been submitted to analysis, there cannot be much doubt from analogy that they will prove to be compound ureas, containing the formyl- and thioformyl-groups respectively.

University of Berlin.

LXXVI.—*Action of Phenyl Cyanate on Polyhydric and certain Monohydric Alcohols and Phenols.*

By H. LLOYD SNAPE, B.Sc.

DURING the course of the research which resulted in the discovery of phenyl cyanate as far back as 1850, Professor Hofmann pointed out the property possessed by this compound of fixing a molecule of either methyl, ethyl, or amyl alcohol, thus producing the phenyl-urethanes of the methyl, ethyl, or amyl series (*Ann. Chem. Pharm.*, **74**, 16). At a later period he showed that phenyl cyanate combines also with

phenol, giving rise to beautiful crystals of the phenyl-urethane of the phenyl series, (*Ber.*, 4, 249).

The behaviour of phenyl cyanate with polymeric alcohols and phenols had not yet been examined. Phenyl cyanate having of late, by the introduction of phosgene gas into the manufacture of aniline colours, become more accessible to chemists, Professor Hofmann suggested to me to engage in an inquiry of this description, and inserted in the *Berichte der deutschen chemischen Gesellschaft* (1885, 518), a note communicating the first result I had obtained, viz., with resorcin, stating at the same time the direction in which I was working.

Since then, in the same journal (*Ber.*, 1885, 968), a paper has been published by H. Tessmer, who has there described the action of phenyl cyanate upon glycerine, erythrite, mannite, and dulcite, some of which substances I had already commenced to examine, and thus the scope of my inquiry has been considerably limited.

The phenyl cyanate combined in most cases readily with the phenol or alcohol on heating the mixture in a sealed tube at 100° from 10 to 16 hours. If the heating is not continued so long, the yield is less; and in no case, although I tried if other temperatures and longer heating were more favourable, did I succeed in obtaining complete combination. There was always an odour of phenyl cyanate evolved by the crude product, and a not inconsiderable loss, in separating from the substances which had escaped reaction; the pure recrystallised urethane varied from 12 to 64 per cent. of the theoretical yield.

The combination, in all the cases I examined, took place so as to form a urethane, viz., in the proportion of 1 mol. phenyl cyanate to each OH group in the phenol or alcohol. That an allophanate was not formed was perfectly evident in each case from the percentage composition.

The new compounds are generally white crystalline compounds, insoluble in water, but readily soluble in alcohol, ethyl acetate, ether, and chloroform. On heating, they first melt, and then decompose into their original constituents.

Resorcin Phenyl-carbamate, $C_6H_4(O\cdot CO\cdot NH\cdot C_6H_5)_2$.

Resorcin and phenyl cyanate, in the proportion of 1 to 2 mols. respectively, were heated in a sealed tube at 100° for 10 hours. The crude product was a yellow crystalline mass. This was washed with cold alcohol until free from phenyl cyanate, and then recrystallised from boiling alcohol. In this way beautiful plates with trapezoidal faces were obtained. From a chloroform solution, tufts of needles

were deposited melting at 164°. It is insoluble in water and in light petroleum, readily soluble in alcohol and ethyl acetate, somewhat less soluble in ether, benzene, and chloroform.

It decomposes under the influence of heat into resorcin and phenyl cyanate.

	Found.		Calculated for $C_6H_4(O\cdot CO\cdot NH\cdot C_6H_5)_2$.
C	68.59	68.73	68.96
H	5.07	4.77	4.60
N	—	8.09	8.05

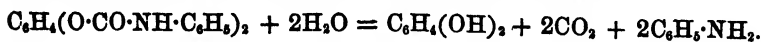
Pyrocatechin Phenyl-carbamate, $C_6H_4(O\cdot CO\cdot NH\cdot C_6H_5)_2$.

Pyrocatechin was similarly treated with phenyl cyanate in a sealed tube at 100°. The contents of the tube after heating consisted of yellowish-white crystals smelling strongly of phenyl cyanate. These were washed with light petroleum to remove the cyanate, and re-crystallised from hot dilute alcohol. The pure substance was deposited in well-formed needles of melting point 165°. It is insoluble in water, readily soluble in alcohol, ethyl acetate, ether, and chloroform, less soluble in benzene and light petroleum.

On heating, the crystals decompose into phenyl cyanate and pyrocatechin.

	Found.	Calculated for $C_6H_4(O\cdot CO\cdot NH\cdot C_6H_5)_2$.
C	68.60	68.96
H	4.76	4.60
N	8.17	8.05

The almost identical melting points of the resorcin and pyrocatechin derivatives suggested the possibility that they were identical. Differences in behaviour with regard to solvents—the pyrocatechin, for example, was much more soluble in alcohol than the resorcin-derivative—proved, however, that this was not the case. That the two compounds were quite distinct was further shown on heating them with hydrochloric acid in a sealed tube at 150°. The resorcin-derivative was much more difficult to decompose, and it was necessary to heat it to 200° to obtain an appreciable reaction. They were decomposed into carbonic anhydride, aniline, and the dihydroxy-benzene from which they had been respectively prepared.



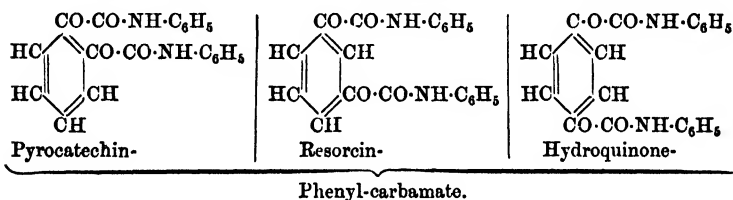
Hydroquinone Phenyl-carbamate, $C_6H_4(O\cdot CONH\cdot C_6H_5)_2$.

Hydroquinone was heated, in the same proportions, with phenyl cyanate in a sealed tube at 100°.

The crude white crystalline product was washed with cold alcohol to remove uncombined phenyl cyanate, and recrystallised from boiling alcohol, of which a large quantity was required for solution. It crystallises in prisms. The melting point was difficult to determine *precisely*. It was about 205–207°, but at 200° the compound rapidly becomes very dark coloured, and decomposes. Its behaviour towards solvents was similar to that of the resorcin-derivative, except that the hydroquinone compound is insoluble in benzene. By heating, the substance is decomposed into phenyl cyanate and hydroquinone.

	Found.	Calculated for $C_6H_4(O\cdot CO\cdot NH\cdot C_6H_5)_2$.
C	68.57	68.96
H	4.74	4.60
N	8.71	8.05

The constitution of the three isomerides would be thus expressed :—



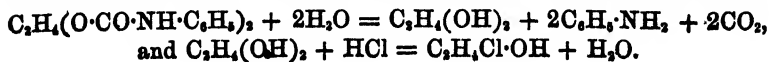
Glycol Phenyl-carbamate, $C_2H_4(O\cdot CO\cdot NH\cdot C_6H_5)_2$.

Crystals were formed, accompanied by considerable development of heat, on mixing glycol and phenyl cyanate at ordinary temperatures; and on heating in a sealed tube at 100° the liquid mixture became almost solid; the white crystalline mass had only a very slight odour of phenyl cyanate. It was recrystallised from boiling alcohol, separating in prisms which, when pure, melted at 157.5°. It is insoluble in water and in light petroleum, soluble in alcohol, ethyl acetate, ether, chloroform, and benzene.

By heating in an open tube, the crystals are sublimed with partial decomposition.

	Found.	Calculated for $C_2H_4(O\cdot CO\cdot NH\cdot C_6H_5)_2$.
C	63.73	64.00
H	5.70	5.34
N	9.59	9.33

By heating with concentrated hydrochloric acid in a sealed tube at 200°, aniline, carbonic anhydride, and glycol chlorhydrin were formed.



Pyrogallol Phenyl-carbamate, $C_6H_3(O\cdot CO\cdot NH\cdot C_6H_5)_3$.

Pyrogallol and phenyl cyanate, in the proportion of 1 mol. of the former to 3 mols. of the latter, were heated for 16 hours in a sealed tube at 100° . The crude product consisted principally of a yellow powder, a portion of which had fused to a light-brown resin. Intimately mixed with the powder was also an oily body from which it was exceedingly difficult to separate. The whole was washed with light petroleum to free it from uncombined phenyl cyanate, and recrystallised from a mixture of alcohol and ether. A white crystalline powder, consisting mainly of minute needles, was thus obtained; melting point 173° . It is coloured brown on exposure to the air, its melting point becoming slightly higher. The brown oxidation product can, however, be washed out by a *little* alcohol. The alcohol-washed compound was dried in a vacuum for analysis. It is insoluble in cold water; by boiling water it is partly decomposed, pyrogallol passing into solution. It is very soluble in alcohol and ethyl acetate, less soluble in ether, benzene, and chloroform, and insoluble in light petroleum.

	Found.		Calculated for $C_6H_3(O\cdot CO\cdot NH\cdot C_6H_5)_3$.
C	—	67.02	67.08
H	—	4.63	4.35
N	8.76	9.11	8.69

This substance burns with difficulty, but good results were obtained on employing lead chromate instead of copper oxide. By heating alone in an open tube, the powder is decomposed into pyrogallol and phenyl cyanate. It is insoluble in cold sodic hydrate solution, and does not reduce silver solutions. On boiling with sodic hydrate solution, it is readily decomposed (much more quickly than by water alone), the liquid becoming dark brown.

Salicyl aldehyde I also submitted to the action of phenyl cyanate in a sealed tube at 100° to ascertain whether the OH group in the former would be attacked similarly to that in phenol. Although combination evidently took place, the fluid mixture being converted into a mass of brown crystals, I was not successful, despite repeated attempts, in obtaining a substance of constant melting point. The difficulty was to obtain a good crystallising medium. Dilute alcohol appeared to best serve this end; and after removing the excess of salicyl aldehyde by sodium hydrate, I recrystallised from this solvent. The recrystallisation was, however, attended with serious loss. I submitted a small portion, whose melting point was $226\text{--}227^\circ$ (that of the previous crystallisation being 224°), to analysis. The percentage composition

indicated a mixture of the urethane and carbanilide. Probably, in the course of recrystallising from dilute alcohol, the urethane is slowly decomposed into its original constituents, and the phenyl cyanate further changed into carbanilide.

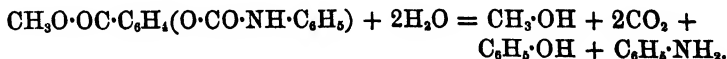
An attempt to form a urethane by the action of phenyl cyanate on salicylic acid was equally unsuccessful. The product, after being washed free from phenyl cyanate by light petroleum and recrystallised from alcohol, readily gave a large quantity of pure carbanilide. Water had apparently been eliminated from the salicylic acid, and this converted the phenyl cyanate into carbanilide. It seemed less probable that water would be formed in this way if an alkyl radicle were substituted for the hydrogen in the carboxyl-group. Hence, I next made an experiment with methyl salicylate.

Methyl Salicylate Phenyl-carbamate, $\text{CH}_3\cdot\text{OOC}\cdot\text{C}_6\text{H}_4(\text{O}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5)$.

Reaction in this case did not take place at 100° , nor even at 150° ; but on heating equivalent proportions of methyl salicylate and phenyl cyanate in a sealed tube at 160° , the greater part of the liquid mixture was converted into beautiful long needles. The crystals were separated from the liquid, and recrystallised from boiling alcohol, of which a large quantity was required for solution. The purified substance was deposited in beautiful long needles, which melted at 238° . It is insoluble in water, soluble in alcohol, ethyl acetate, chloroform, benzene, and ether, very slightly soluble in light petroleum. On heating, the crystals melt and sublime in needles almost without any decomposition.

	Found.	Calculated for $\text{CH}_3\cdot\text{OOC}\cdot\text{C}_6\text{H}_4(\text{O}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_5)$.
C	66.23	66.42
H	5.22	4.80
N	5.87	5.16

The constitution of this compound was further shown by its products of decomposition with hydrochloric acid in a sealed tube at 200° . Aniline, carbonic acid, phenol (recognised by conversion into tribromophenol), and methyl alcohol were formed.



Whilst working upon salicylic acid, the question suggested itself whether the OH of the COOH group in acids could also be similarly acted on by phenyl cyanate.

In order to test this, benzoic acid was digested with phenyl cyanate

in a sealed tube at 100° , but no compound was obtained. The only change effected was that a portion of the phenyl cyanate was converted into carbanilide, probably by the abstraction of water from the benzoic acid, which would be thus converted into benzoic anhydride.

Recrystallisation from ether of the crude substance washed with light petroleum separated merely carbanilide and benzoic acid, the former being much less soluble in ether than the latter.

The two isomeric naphthols reacted with phenyl cyanate in a manner analogous to phenol, yielding a pair of isomeric urethanes.

α -Naphthyl Phenyl-carbamate, $C_{10}H_7\alpha(O\cdot CO\cdot NH\cdot C_6H_5)$.

α -Naphthol and phenyl cyanate were mixed in molecular proportions, and exposed to 100° in a sealed tube. The product, recrystallised from boiling alcohol, yielded acicular crystals, which melted at 178.5° . It is insoluble in water and in light petroleum, readily soluble in alcohol, ethyl acetate, ether, chloroform, and benzene; insoluble in sodic hydrate solution. On heating, it melts and decomposes into α -naphthol (which sublimes) and phenyl cyanate.

	Found.	Calculated for $C_{10}H_7(O\cdot CO\cdot NH\cdot C_6H_5)$.
C	77.32	77.57
H	5.24	4.94
N	5.98	5.32

β -Naphthyl Phenyl-carbamate, $C_{10}H_7\beta(O\cdot CO\cdot NH\cdot C_6H_5)$.

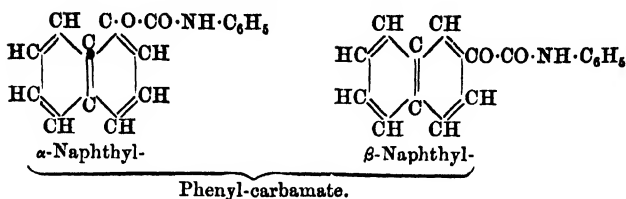
Phenyl cyanate was similarly treated with β -naphthol. The crude mass was first washed with cold alcohol to remove free phenyl cyanate, and then recrystallised from alcohol. After the preliminary washing with alcohol, the substance was almost pure: the quantity of pure substance obtained was 64 per cent. of the theoretical yield. It crystallises in plates, which melt at 155° .

Its behaviour towards solvents is the same as that of the α -naphthol-derivative, except that the β -naphthol phenyl-urethane is sparingly soluble in light petroleum.

The effect of heat is also similar. Decomposition into β -naphthol (which sublimes) and phenyl cyanate takes place.

	Found.	Calculated for $C_{10}H_7(O\cdot CO\cdot NH\cdot C_6H_5)$.
C	77.18	77.57
H	5.32	4.94
N	5.61	5.32

The constitution of the isomerides would be thus expressed:—



Finally, the action of eugenol upon phenyl cyanate was examined, and it was found that this somewhat complex phenol formed also a urethane without any disturbance in the molecule.

Eugenol Phenyl-carbamate, $C_8H_8 \cdot C_6H_5(OCH_3) \cdot O \cdot CO \cdot NH \cdot C_6H_5$.

Eugenol and phenyl cyanate, in molecular proportions, were heated in a sealed tube for 10 hours at 100° . Crystals were formed, but these were mixed with large quantities of uncombined eugenol and phenyl cyanate.

On pressing the crystals between filter-paper, and then passing a current of dry air through the melted product (in a water-bath), the purified crystals amounted to only 38 per cent. of the theoretical yield. Heating to between 120° and 150° appeared to be even less conducive to obtaining a good yield. Possibly a slightly lower temperature than 100° might have produced more complete combination.

The crystals, thus freed from excess of eugenol and phenyl cyanate, were readily purified by recrystallisation from light petroleum. It forms needles which melt at 95.5° . It is insoluble in water, readily soluble in alcohol, ethyl acetate, ether, chloroform, and benzene, somewhat less soluble in light petroleum. On heating, it sublimes with partial decomposition into eugenol and phenyl cyanate.

	Found.	Calculated for $C_8H_8 \cdot C_6H_5(OCH_3) \cdot O \cdot CO \cdot NH \cdot C_6H_5$.
C	72.17	72.08
H	6.27	6.01
N	5.41	4.95

Lastly, I examined the action of phenyl cyanate on a thiophenol. This had not been previously investigated, although Hofmann performed a precisely analogous reaction in the fatty series, by treating ethyl isocyanate with ethyl mercaptan, thus obtaining an ethyl thio-ethyl-urethane (*Ber.*, 2, 118), $C_2H_5 \cdot S \cdot CO \cdot NH \cdot C_2H_5$.

The isomeride in which the atoms of sulphur and oxygen exchange places (*i.e.*, the body having the constitution $C_2H_5 \cdot O \cdot CS \cdot NH \cdot C_2H_5$) was also prepared by Hofmann by the action of ethyl isothiocyanate on alcohol (*Ber.*, 2, 117).

Hofmann showed further that allyl (*Ber.*, **2**, 119) and phenyl (*ibid.*, 120) isothiocyanates, in contact with ethyl alcohol, yielded analogous compounds.

Phenyl Phenyl-thiocarbamate, $C_6H_5(S \cdot CO \cdot NH \cdot C_6H_5)$.

The phenyl mercaptan, required for my experiment, was prepared by the method first given by Schiller and Otto (*Ber.*, **9**, 1586, and **10**, 940—941), 75·4 per cent. of the theoretical yield being thus obtained.*

Phenyl mercaptan and phenyl cyanate, in molecular proportions, were heated in a sealed tube for 15 hours at 100°. The combination was not complete, but on pressing the very beautiful crystals (needles) which had formed between filter-paper, they were obtained almost pure. They were recrystallised from boiling alcohol, when long needles melting at 125° were obtained. The crystals possess a faint odour of phenyl mercaptan. They are insoluble in water, readily soluble in alcohol, ethyl acetate, ether, chloroform, and benzene, less soluble in light petroleum.

On heating, the crystals sublime in long needles, with simultaneous partial decomposition into phenyl mercaptan and phenyl cyanate.

This compound is not so readily oxidised as phenyl mercaptan. Thus when boiled for a few minutes with ferric chloride solution, only a trace of ferrous salt was produced, and potassium dichromate solution was not turned green under similar circumstances. On boiling with potassium permanganate solution, it was decolorised. The crystals dissolved in concentrated sulphuric acid, and, on warming, a blue colour, like that first obtained by Baumann and Preusse (*Zeit. physiol. Chem.*, **5**, 321) from phenyl mercaptan under similar treatment, was produced.

	Found.		Calculated for $C_6H_5(S \cdot CO \cdot NH \cdot C_6H_5)$.
C	68·58	—	68·12
H	4·69	—	4·80
N	6·81	—	6·11
S	14·29	14·37	13·98

In order to estimate the quantity of sulphur present, it was necessary to heat in a sealed tube with fuming nitric acid to 270°.

Besides the isomeric ethyl thioethyl-carbamates already mentioned,

* I should not leave unmentioned that, with the exception of the phenyl cyanate, which I obtained through the kindness of Messrs. Hofmann and Schoetensack, Ludwigshafen-am-Rhein, all the chemical compounds that I required in the course of this work, were obtained in a state of purity (as shown by melting and boiling points) from Kahlbaum's manufactory.

two methyl thiocarbamates ($\text{CH}_3\cdot\text{S}\cdot\text{CO}\cdot\text{NH}_2$,* and $\text{CH}_3\cdot\text{O}\cdot\text{CS}\cdot\text{NH}_2$ †) and the two corresponding ethyl ethers ($\text{C}_2\text{H}_5\cdot\text{S}\cdot\text{CO}\cdot\text{NH}_2$,‡ and $\text{C}_2\text{H}_5\cdot\text{O}\cdot\text{CS}\cdot\text{NH}_2$ §) are known.

It would be interesting to prepare and compare with the above body the isomeride, $\text{C}_6\text{H}_5(\text{O}\cdot\text{CS}\cdot\text{NH}\cdot\text{C}_6\text{H}_5)$. One would expect this to result from the action of phenyl thiocyanate on phenol; but I have not yet attempted to carry out this reaction.

It would also be interesting to compare the action of phenyl cyanate on the phenylene dihydrosulphides with that on the dihydroxybenzenes.

LXXVII.—*Chemical Examination of the Constituents of Camphor Oil.*

Communication from the Chemical Society of Tokio by HIKOROKURO YOSHIDA, Chemist to the Imperial Geological Survey.

ESSENTIAL oil of camphor is obtained by distilling camphor wood (*Laurus camphora*) with water, when it comes over together with a steoptene, the laurel camphor.

Camphor tree grows abundantly in the Islands of Kinshû and Shikoku, especially on the warm southerly sea-coast in those parts. Kioshu, Shiznoka, Dewa, and some other places also furnish large quantities of camphor tree.

Older trees contain a much larger amount of the camphor and the oil than young ones, and when several hundred years of age they are so enriched with these substances that the crystals of the camphor are often found deposited on the bark of the tree, and near the ground where it grows. For a profitable extraction of the camphor, however, the trees must be over 200 years old. The camphor and the oil are not found equally distributed throughout all parts of the tree; the main stem and the root contain them in the greatest abundance, whilst there is but little in the small branches and leaves; again, the relative proportion of the steoptene and the oleoptene differ in different trees.

To obtain the camphor and the oil, the wood is rather finely chopped, and put at once into stills along with water and distilled; the yield of the crude product amounts to about 3 per cent. of the wood

* Blankenhorn, *J. pr. Chem.* [2], 16, 375.

† Salomon, *J. pr. Chem.* [2], 8, 115.

‡ Salomon, *J. pr. Chem.* [2], 7, 256.

§ Debus, *Annalen*, 72, 11.

employed. The camphor which crystallises out from the oil is separated by pressing it in a linen bag; the oil which flows out is next distilled in a retort until about two-thirds of it comes over, the residue is again cooled and pressed; and these processes are repeated in succession until the camphor left dissolved in the oil is reduced to a comparatively small amount. The following* is a *résumé* of the yield of these substances in one of the Tosa factories:—

Summer yield, a day's working,—120 kilos. of wood give 2.4 kilos. of camphor and 1.8 litres of the oil.

Winter yield, a day's working.—The same quantity of wood gives 3 kilos. of camphor and 0.5—0.7 litre of the oil.

The oil upon which I worked consisted of two different specimens. The one was five years old, and the other much more recent, although its exact age could not be ascertained; they jointly amounted to a little over 4 gallons. The oil was yellowish, with a strong characteristic camphoraceous odour and hot burning taste; the sp. gr. of the more recent oil was 0.9432, and of the older one 0.9505 at 15°. Both of them were very slightly acid in reaction, and deposited some camphor when cooled in a freezing mixture, the amount of which was about one-third greater in the old than in the recent specimen. The oil absorbs oxygen from the air, thereby acquiring a deeper colour. About 50 c.c. of the freshly-distilled oil (boiling point = 160—217°, and freed from the dissolved camphor by cooling) was put in a eudiometer together with oxygen and allowed to stand over mercury in a sunny place. At the end of a month, about 4 c.c. of oxygen was found to have been absorbed, and on examining the oil with starch and potassium iodide paper a distinct blue colour was developed after some time; on cooling the oil, a small quantity of camphor was also deposited. This shows that the effect of the ageing of the oil in presence of oxygen is to produce some camphor, probably at the expense of the other constituents, which, as I shall hereafter explain, are two terpene hydrocarbons and an oxygenated oil of the composition $C_{10}H_{16}O_2$. In preserving the oil, it is therefore quite necessary to keep it in a well-closed vessel, full; and as far as possible to avoid access of air.

Chlorine and bromine act powerfully on the oil, and if the temperature is allowed to rise during the reaction, a good deal of hydrochloric or hydrobromic acid is evolved, and the oil is ultimately converted into a dark viscous mass. The oil when mixed with sulphuric acid becomes heated, and gives a good deal of sulphurous acid, the product being gradually charred. If a moderately strong acid is employed, the mixture allowed to stand for some hours and then distilled with steam, an oily matter is obtained from which some camphor separates out on cooling; some cymene is also found in the product, being produced

* "On Camphor Oil," by Oishi.

probably from the terpene by Ribau's reaction. Concentrated nitric acid acts most energetically on the oil, with production of a yellow oil which gradually disappears, and if the action be continued with occasional addition of fresh acid until red fumes cease to appear, and the solution concentrated, a crystalline substance is finally produced. This substance gave the reactions for camphoric acid with zinc, lead, and mercury salts, all of which are very characteristic. The production of this acid from the oil can be traced to the oxidation of the compound $C_{10}H_{18}O_2$, and also some camphor present in it. The camphor oil absorbs a good deal of hydrogen chloride. The product of this reaction, which is a dark-coloured oil, does not bear distillation, and it appears that if any definite hydrochloride were produced at first, it is decomposed during the process of distillation into hydrogen chloride and an oil in which the polymerides of the original constituents abound.

The camphor oil is miscible in almost every proportion with ether, chloroform, absolute alcohol, and most of the essential oils; it also dissolves several resins, such as colophony, gum elemi, mastic, balsam and asphalt, and the experiments made in this direction by Mr. Oishi show that this property renders it fit for the preparation of varnishes.

Before proceeding to record the details of the present experiments it will be well here to mention the two important publications on the subject. The one is by Beckett and Wright, "On the Oil from Camphor Sublimation" (*Chem. Soc. J.*, 1876, 7), in which they find the composition of that portion of the oil boiling at 170° to be represented by $5(C_{10}H_{14}) + C_{10}H_{18}O$. The other is by Oishi, "On Camphor Oil," being a graduating thesis written in 1883 at Tokio University. Oishi analysed two fractions of the oil, collected respectively at 178° — 180° and 180° — 185° ; for the composition of the lighter fraction, he obtained $C = 86.95$ per cent. and $H = 12.28$ per cent., and the vapour-density 5.70 , from which he deduces the formula $C_{12}H_{20}$.

The numbers obtained for the fraction 180° — 185° are $C = 78.87$ per cent. and $H = 10.73$, and he concluded it to be a "liquid isomer of camphor," $C_{10}H_{18}O$; these results will, however, be discussed in connection with mine towards the end of this paper.

On submitting the oil to a prolonged distillation, a small quantity of it came over below 150° , but the greater portion distilled between this temperature and 215° . By this treatment the oil suffers a good deal of decomposition and some polymerisation, like other essential oils, and it also deposits a great quantity of solid camphor in the higher fractions of the distillate, which was all removed by pressing in a linen bag, after thoroughly cooling by a freezing mixture. Omitting all the details of the fractional distillation of the oil, except to say

that the total number of fractionings was about 65, and that it was partly conducted in an ordinary retort and partly with Le Bel's apparatus, it was finally separated into four different fractions, which boiled at the constant temperatures named below.

- (1.) A hydrocarbon (terebenthene), b. p. 156°.
- (2.) A hydrocarbon (probably citrene), b. p. 172—173°.
- (3.) Camphor, 205°.
- (4.) An oxygenated oil (camphorogenol), 212—213°.

The intermediate fractions finally obtained were very small, and they might have been further separated into the portions named above had it not been an unprofitable work.

There is besides the substances mentioned, a very small quantity of an oily hydrocarbon boiling below 145°, but its exact nature could not be ascertained, owing to the scarcity of the material at my disposal, and the consequent difficulty of isolating it in a pure state; the work done and recorded in the following pages, therefore, is confined to all the constituents of the camphor oil, except the lightest oil just named and also the camphor.

It is rather difficult to state accurately the amount of the various substances present in the oil, inasmuch as its composition changes with its age; moreover, it suffers decomposition during distillation. Roughly speaking, however, the composition of the lately examined oil (five years old) may be fixed as follows:—

The lightest oil, b. p. below 145°	0·2 per cent.
Terebenthene	7·0 „
Citrene	20·0 „
Camphor	22·8 „
Camphorogenol	50·0 „
	<hr/>
	100·0

The hydrocarbon boiling at 156°, present in the camphor oil, was found to be identical with terebenthene. Just as various terebenthenes obtained from various species of *Pinus* differ in some of their physical properties, such as odour and optical activity, from each other, so does the camphor oil terebenthene show differences of this kind, but these can be regarded more as physical than chemical differences, inasmuch as the action of various reagents on them is identical.

Camphor oil terebenthene, rectified over sodium, is a very mobile liquid of an agreeable characteristic odour, which is milder than either of the terebenthenes from various turpentine oils. It has a very strong lævorotatory action on polarised light, being perhaps the most active of all the terebenthenes known; tested with Hof-

mann's polarimeter, it showed the specific rotatory power of $[\alpha]_D = -76.1^\circ$; its density at 15° is 0.8641.

It is readily soluble in chloroform, benzene, carbon bisulphide, and absolute alcohol, but with ether it forms a turbid mixture.

Combustion of the substance gave the following results:—

- I. 0.3210 gram substance gave 1.0372 gram CO_2 and 0.3437 gram H_2O .
 II. 0.2240 gram substance gave 0.7246 gram CO_2 and 0.2386 gram H_2O .
 III. 0.3052 gram substance gave 0.9811 gram CO_2 and 0.3242 gram H_2O .

	I.	II.	III.	Mean.	$\text{C}_{10}\text{H}_{16}$.
Carbon	88.12	88.22	88.30	88.21	88.23
Hydrogen ..	11.89	11.83	11.80	11.84	11.76
				<hr/> 100.05	<hr/> 100.00

The hydrocarbon readily combines with hydrogen chloride, forming beautifully crystalline compounds. A slow current of dry hydrogen chloride was led into the hydrocarbon kept cool in a freezing mixture until it was saturated with the gas. Keeping the liquid cool, a pasty mass of crystals was obtained after some time; these, quickly collected, well pressed, and thrice recrystallised from absolute alcohol, gave beautiful colourless crystals of terebenthene hydrochloride.

The chlorine determined by Carius' method gave the following numbers:—

- I. 0.4322 gram substance gave 0.3550 gram AgCl .
 II. 0.5215 ,, ,, 0.4302 ,,

	I.	II.	Mean.	Terebenthene hydrochloride, $\text{C}_{10}\text{H}_{16}, \text{HCl}$.
Chlorine ..	20.31	20.40	20.36	20.46

The melting point of this substance determined by Ribau's method, that is to say, in a sealed tube in an atmosphere of dry hydrogen chloride, gave the number $130-131^\circ$. Terebenthene hydrochloride resembles common camphor in appearance and also in odour, but this is not quite so sharp as that of the latter; it crystallises in white grains or needles, which are readily soluble in alcohol or ether, but insoluble in water, and when the compound is distilled with the latter fluid, it is slowly converted into an optically inactive terpene (terebene?) with elimination of hydrochloric acid.

The mother-liquor separated from the crystals of terebenthene

hydrochloride consisted of impure liquid hydrochlorides, as Ribau (*Compt. rend.*, 88) has also shown to be the case with terebenthene from French turpentine, but the difficulty of isolating any pure compound from it rendered the working at it rather unpromising, and its study has been discontinued for the present.

The camphor oil terebenthene yielded its dihydrochloride in a crystalline state, when the hydrocarbon was treated in a manner somewhat different from the one just described. The hydrocarbon was mixed with an equal volume of ether containing a small quantity of absolute alcohol, the solution well cooled and then saturated with dry hydrogen chloride; the resulting liquid was transferred to a beaker, and the ether evaporated at a gentle heat. On cooling the liquid to about -10° for some time, it became filled with a mass of crystals of the dihydrochloride; these were quickly collected by means of a vacuum pump, the mass well pressed, and then purified by recrystallisation from ether.

The pure terebenthene dihydrochloride thus obtained is apparently rhombic in form, of a faint peculiar odour, insoluble in water, but readily soluble in ether or alcohol. If it be heated with alcohol at 100° for many hours, or if the temperature of the liquid be allowed to rise much above 0° during the preparation, the dihydrochloride will be found to be very difficult to separate by crystallisation. The melting point of the compound determined in an atmosphere of hydrogen chloride is $48-49^{\circ}$.

The substance on analysis gave the following amount of chlorine :—

- I. 0.3216 gram substance gave 0.4398 gram AgCl.
 II. 0.2243 „ „ 0.3074 „

	I.	II.	Mean.	$C_{10}H_{16}, 2HCl.$
Chlorine . .	33.83	33.89	33.86 p. c.	33.97 p. c.

One of the most beautiful and sensitive reactions of this compound, first observed by Ribau (*Compt. rend.*, 78), is the production of a rich rose colour, when a few crystals of the dihydrochloride are triturated with a drop of strong ferric chloride solution, and the whole gently warmed; the rose colour first produced soon changes to reddish-violet and finally to blue.

An attempt was made to ascertain whether solid terebenthene monohydrochloride once produced can be changed into the dihydrochloride by the further action of hydrogen chloride; the result, however, was negative.

The monohydrochloride is converted into solid camphene by the action of soda; the dihydrochloride is, by the same treatment, changed chiefly into terpinol; and these facts show, as Tilden remarks

(*Chem. Soc. J.*, 1878, 249), that the constitution of the two hydrochlorides must be essentially different.

One of the most important derivatives of a terpene is its nitroso-compound described by Tilden and Shenstone (*Chem. Soc. J.*, 1877, 555), inasmuch as the examination of its properties may serve amongst other things for the classification of a large number of terpenes described by various authors. To begin with, nitrosyl sulphate was prepared by Tilden's method (*Chem. Soc. J.*, 1874, 631). The gases evolved from aqua regia mixture (4 measures HCl of sp. gr. 1.16 + 1 measure of HNO_3 sp. gr. 1.42) was dried by calcic chloride, and then passed into concentrated sulphuric acid kept cool by ice, until it was saturated with nitric oxide gas. The solution obtained consists mainly of acid nitrosyl sulphate, which when acted on by fused sodic chloride moistened with strong hydrochloric acid, readily yields gaseous nitrosyl chloride, NOCl , in an almost pure state.

About 120 grams of camphor oil terebenthene was dissolved in twice its volume of absolute alcohol, the whole kept cool in a freezing mixture, and a slow current of nitrosyl chloride gas passed into it so long as white granular crystals continued to be deposited, the solution becoming bright green. To obtain a regular flow of the gas from the generator, it is best to drop the nitrosyl sulphate solution gradually on to the sodic chloride from the narrow point of a funnel tube, and after some time to warm gently. It is very necessary that in this experiment the hydrocarbon solution should be kept well cooled, as in the preparation of the hydrochlorides, since the success of the experiment depends greatly on the temperature at which the reaction takes place; if it be allowed to rise a little above 0° , the crystals of terpene nitrosochloride already formed are liable to be rapidly destroyed. To secure the compound, the contents of the bottle were mixed with further quantities of absolute alcohol, allowed to stand for half an hour in a freezing mixture, and filtered; the crystals of nitrosochloride of terebenthene were then thoroughly washed with absolute alcohol, redissolved in chloroform, reprecipitated with absolute alcohol, collected and finally dried at a low heat; the yield of the substance was about 20 per cent. of the hydrocarbon employed.

The nitrosochloride of terebenthene is a beautifully white crystalline powder, almost odourless, sparingly soluble in absolute alcohol, and unaffected by water or soda solution; it is soluble in chloroform, benzene and ether, but the compound cannot be recrystallised from those solvents without undergoing slight decomposition. The following numbers were obtained on analyses:—

I. 0.4204 gram substance gave 0.9107 gram CO_2 and 0.3061 gram H_2O .

II. 0.3345 gram substance gave 0.7289 gram CO_2 and 0.2142 gram H_2O .

III. 0.4236 gram substance gave 0.2964 AgCl .

IV. 0.2173 " " 0.1537 "

V. 0.4196 gram substance gave 26 c.c. of nitrogen at 15° and 768.3 mm. pressure.

	I.	II.	III.	IV.	V.	Mean.	$\text{C}_{10}\text{H}_{16}\text{NOCl}$.
Carbon ..	59.09	59.43	—	—	—	59.27	59.55
Hydrogen	8.09	8.01	—	—	—	8.05	7.94
Nitrogen.	—	—	—	—	7.42	7.42	6.94
Chlorine.	—	—	17.30	17.48	—	17.39	17.60
Oxygen..	—	—	—	—	—	7.87	7.97
						<hr/> 100.00	<hr/> 100.00

When the above compound is gently heated with alcoholic soda or potash, in which it dissolves, a reaction takes place of which the elements of hydrogen chloride are removed from the compound, forming nitrosoterebenthene, $\text{C}_{10}\text{H}_{16}\text{NO}$. On neutralising the alkaline solution with acetic acid, evaporating to dryness, exhausting the residue with water, and then dissolving the product in alcohol, and evaporating, large crystals of the compound are deposited, the form of which is very characteristic. The following numbers were obtained :—

I. 0.4235 gram substance gave 1.1278 gram CO_2 and 0.3511 gram H_2O .

II. 0.3451 gram substance gave 0.9184 gram CO_2 and 0.2850 gram H_2O .

III. 0.3921 gram substance gave 28 c.c. N at 15°C . and 769 mm. pressure.

	I.	II.	III.	Mean.	$\text{C}_{10}\text{H}_{16}\text{NO}$.
Carbon	72.62	72.58	—	72.60	72.72
Hydrogen ..	9.21	9.17	—	9.19	9.09
Nitrogen ...	—	—	8.56	8.56	8.48
Oxygen	—	—	—	9.65	9.71
				<hr/> 100.00	<hr/> 100.00

Nitrosoterebenthene is soluble both in warm caustic soda solution and in concentrated sulphuric acid, and is precipitated unchanged either by neutralisation or dilution with water; it is also soluble in ether, alcohol, &c., but insoluble in water. The melting point of the substance determined in a capillary tube is 130° . When heated, it sublimes without decomposition, and in fact it is one of the most stable derivatives of terebenthene. The second compound in order of

the boiling point, present in camphor oil, is a terpene hydrocarbon, having a pleasant odour of lemon oil. After the most tedious processes of fractional distillation aided by purification with sodium it was found to boil constantly at 172–173°. This hydrocarbon is probably chemically identical with citrene; the main constituent of the so-called essence of lemon. The point of difference from the lemon oil citrene is its levorotatory power, viz., $[\alpha]_D = -68.3^\circ$, but this, as was before remarked, can be looked upon as a physical difference between the two, such cases being common among the optically active terpenes. Its density is $D_{20}^{20} = 0.8733$. The analyses gave the following results:—

I. 0.3621 gram substance gave 1.1699 gram CO_2 and 0.3916 gram H_2O .

II. 0.3053 gram substance gave 0.9874 gram CO_2 and 0.3252 gram H_2O .

	I.	II.	Mean.	$\text{C}_{10}\text{H}_{16}$.
Carbon. . . .	88.08	88.21	88.15	88.23
Hydrogen . .	12.00	11.83	11.91	11.77
			<hr/> 100.06	<hr/> 100.00

A search for cymene in this hydrocarbon, by treating it with sulphuric acid (1:4), steam-distilling it, and then oxidising the very small quantity of oily matter obtained with strong chromic acid mixture, gave no terephthalic acid, showing the absence of cymene in the terpene examined.

By saturating an ethereal solution of the citrene kept at -10° with dry hydrogen chloride, and treating the product in the same way as in the case of terebenthene, the dihydrochloride of citrene was easily obtained. Purified by recrystallation from ether at a low temperature, the compound was obtained in glistening rhombic crystals which appeared very similar to those of terebenthene dihydrochloride. The melting point of this substance was $58-59^\circ$, being about 10° higher than the corresponding compound from terebenthene. 0.3215 gram substance gave 1.0985 gram AgCl = chlorine 34.00 per cent.; the theory for $\text{C}_{10}\text{H}_{16}, 2\text{HCl}$ requires 33.97 per cent. Cl . An attempt was made to obtain the nitrosyl chloride of the citrene in the same way as with terebenthene, but was unsuccessful; the liquid became bright green after passing the gas for four consecutive hours, and the solution afterwards mixed with a large volume of alcohol and kept cool for many hours, gave no sign of the production of crystals. It would appear that, if a nitrosyl chloride of the citrene is produced in this reaction, it is a liquid body, and cannot be separated from the impure mother-liquor by any method at present known. It

is also impossible, as with citrene from lemon oil, to obtain the monohydrochloride of this hydrocarbon.

A quantity of the citrene was put into a large bottle provided with a reflux condenser and heated with strong chromic acid mixture for two days. A large amount of carbonic acid was evolved during the reaction, and the remaining oily matter was reduced to about one-third of the amount originally taken. This oil separated, dried, and distilled, showed no fixed boiling point; but on repeating the fractionation, the greater part boiled below 178° , and had an odour resembling that of the polymerised citrene oil. The higher fraction collected at 220 — 230° had a pronounced odour of a mixture of orange with a little mint oil. The lower fraction (below 178°) analysed gave numbers which show that it was probably a mixture of an unaltered citrene with an oxidised compound, probably $C_{10}H_{16}O$ (not camphor).

0.3521 gram substance gave 1.1270 gram CO_2 and 0.3727 gram H_2O .

	Found.	Theory for $10(C_{10}H_{16}) + C_{10}H_{16}O$.
Carbon	87.29	87.31
Hydrogen ..	11.76	11.64
Oxygen	0.95	1.05
	<hr/> 100.00	<hr/> 100.00

The fraction 220 — 230° was a somewhat heavy oil, and amounted to about 2 per cent. of the original citrene taken. The numbers obtained by analysis show that the composition of the substance is mainly $C_{10}H_{16}O$, probably the same body obtained by Wright (*Chem. Soc. J.*, 1873, 554) by the oxidation of hesperidine with chromic acid mixture.

0.3213 gram substance gave 0.9235 gram CO_2 and 0.3071 gram H_2O .

	Found.	Theory for $C_{10}H_{16}O$.
Carbon	78.42	78.94
Hydrogen	10.62	10.53
Oxygen	10.96	10.53
	<hr/> 100.00	<hr/> 100.00

This substance cannot be camphor, as judged from its boiling point (boiling point of camphor = 205°), smell, &c.; nor did it deposit any solid camphor on cooling it in a freezing mixture.

On distilling the chromic acid liquor in the bottle, a small quantity of volatile acid was obtained, which was found to be chiefly acetic acid. The residue (half of the liquid) in the retort was carefully

examined for terephthalic acid by treating it with ammonia, neutralising with hydrochloric acid, &c., but gave only negative results.

This experiment shows that camphor oil citrene, like hesperidine, when oxidised with chromic acid liquor, takes up oxygen, forming $C_{10}H_{16}O$, which is *not camphor*, showing that the latter is not produced by the direct oxidation of the citrene in the original oil. A large quantity of carbonic acid and some acetic acid, &c., are also formed during the reaction.

As terpenes are uniformly cymene-derivatives, it was thought possible to obtain the latter hydrocarbon from the camphor oil citrene, by a process by which other terpenes were reduced to cymene. To the hydrocarbon, a solution of bromine in potassic bromide was gradually added, in the ratio of two molecules of bromine to one of the hydrocarbon; the bromine was easily taken up by the oil without any evolution of hydrogen bromide, and the resulting dibromocitrene was colourless and had a peculiar pleasant odour. If this compound is heated, it splits up into cymene and hydrogen bromide, according to the well-known equation, $C_{10}H_{16}Br_2 = C_{10}H_{14} + 2HBr$.

This was readily effected by cohobating the oil for some time, after the water had been separated, and then distilling it a few times. A large quantity of hydrogen bromide was evolved, and the crude cymene collected in the receiver. The distillate was now cohobated with strong soda solution for some time, and then fractionally distilled over sodium. The principal portion of the oil boiled between 175° and 178° , and showed all the characters of cymene. A portion of this cymene was boiled with strong chromic acid mixture for about three days until all the oily matter had disappeared. After cooling, the whole was filtered, the residue washed with water, dissolved in strong ammonia, and then precipitated with hydrochloric acid; the substance thus obtained was terephthalic acid. Purified by repeated solution in ammonia and precipitation with hydrochloric acid, it was a white powder of a peculiar pleasant odour, and only very sparingly soluble in alcohol, water, and ether. The yield of this acid was a little less than 40 per cent. of the cymene employed. Its composition was as follows:

- I. 0.3520 gram substance gave 0.7432 gram CO_2 and 0.1185 gram H_2O .
- II. 0.3316 gram substance gave 0.7010 gram CO_2 and 0.1102 gram H_2O .

	I.	II.	Mean.	Terephthalic acid. $C_8H_6O_4$.
Carbon	57.58	57.65	57.62	57.83
Hydrogen ..	3.74	3.69	3.72	3.62
Oxygen	—	—	38.66	38.55
			<hr/> 100.00	<hr/> 100.00

The study of the action of nitric acid on the citrene does not give promising results, the reaction appearing to be a very complicated one. If a mixture* consisting of $2\frac{1}{2}$ parts by measure of the citrene, with 1 of nitric acid (sp. gr. = 1.4) and 1 of methylated spirit, be put in a shallow dish and exposed to the air, the hydrocarbon becomes thick and acquires an odour of a resinised turpentine, but no terpin is produced by this treatment. When the hydrocarbon is boiled with dilute nitric acid, it is converted into a yellow oil, from which it was very difficult to isolate any definite compounds. It may be remarked here, however, that no camphor is produced in either of these cases, every attempt to detect it being fruitless.

The next experiment was modified in the following way:—To about a pound of strong nitric acid put in a large bottle and provided with a reflux condenser, about 50 grams of citrene was cautiously and gradually added. After the first violent reaction had ceased, the bottle was gently heated, when yellowish resinous matter was formed, the greater part of which, however, disappeared on continuing the action of the acid. At the end of a day's heating, the liquid in the bottle was filtered and evaporated almost to dryness, then rendered alkaline with ammonia, and boiled with addition of calcic chloride solution. A large quantity of fine granular precipitate was produced, which, when collected and thoroughly washed, looked very much like calcic oxalate. Dried at 100° and ignited, it gave 38.42 per cent. of lime, which corresponds to calcic oxalate with a molecule of water, viz., C_2O_4Ca, H_2O , theory requiring 38.36 per cent. of lime. The filtered solution was again evaporated on a water-bath, the residual pasty mass digested with ether alcohol, acidified with sulphuric acid, filtered, and the solution again evaporated, when a small quantity of an acid syrup was obtained. The portion remaining on the filter consisted of a mixture of calcic and ammonic sulphate. As lead acetate gave a yellowish flocculent precipitate with aqueous solution of the syrup, an attempt was made to purify the substance by converting it into a lead salt, and then decomposing it with sulphuretted hydrogen; but the amount obtained after these operations was so small that nothing could be done with it. The only attempt towards ascertaining its composition which I was able to make was the estimation of the amount of barium in a salt produced by neutralising the syrup with basic carbonate. The substance filtered, evaporated, and then dried at 150° , gave an amorphous mass of a light lemon colour, which, on ignition with sulphuric acid, gave 72.54 per cent. of

* Since this paper was written, it has been found that camphor oil terebenthene treated in this manner, gives abundance of terpin crystals. According to Tilden, terpin is also produced from lemon oil terpene, so that camphor oil citrene may be said to differ from it in not yielding the same compound.

$\text{BaSO}_4 = \text{Ba } 46.65$ per cent. Wright has shown (*Chem. Soc. J.*, 1873, 556) that when hesperidine (from orange) is treated in somewhat the same manner, it yields an acid which he called "hesperisic acid," ($\text{C}_{20}\text{H}_{26}\text{O}_{17} \cdot 2\text{H}_2\text{O}$), and this gave a calcium salt which when dried at 160° , had the composition $\text{C}_{20}\text{H}_{12}\text{Ca}_3\text{O}_{13}$. It is likely, therefore, that with camphor oil citrene, a somewhat similar acid is formed in the above reaction, inasmuch as it was produced by a somewhat similar process, and from the two closely allied terpenes, viz., hesperidine and citrene. The number obtained for the barium in the above compound comes near to that required by the barium salt of hesperisic acid, $\text{C}_{20}\text{H}_{12}\text{Ba}_3\text{O}_{13}$, namely, $\text{Ba} = 47.19$ per cent.

When that portion of the oil boiling at $208\text{--}218^\circ$ is carefully fractionated, it finally yields an oxygenated oil boiling at $212\text{--}213^\circ$. This has been found to be the main constituent of the original camphor oil, and the direct source from which camphor is produced. The substance can only be obtained in a pure state by cooling that portion of the fraction boiling at $212\text{--}213^\circ$ to about -30° after each distillation. In this way a small quantity of dissolved camphor is separated, this being inevitably produced in some quantity from the compound during the process of distillation. It was doubtful whether the camphor which thus separates out on cooling after each distillation was contained in the oil ready formed and not quite removed by previous treatments, or whether it was produced by the action of heat on the oil. Several experiments which were made to settle this point, however, proved conclusively that it is produced in the latter way, and is not due to its previous imperfect removal.

(a.) 200 grams of the compound freed from camphor at -30° was slowly distilled with Le Bel's apparatus; the several fractions were collected separately and examined.

24 grams of the substance distilled below 212° .			
133	"	"	at $212\text{--}213^\circ$.
29	"	"	at $213\text{--}220^\circ$.
8	"	"	at $220\text{--}230^\circ$.
6 grams residue in the bottle + loss.			

200 grams.

These distillates were separately cooled in a freezing mixture of ice and powdered calcic chloride crystals at -32° , and the separated camphor was rapidly collected on a vacuum filter, well pressed and weighed.

The fraction below 212° gave 3.2 grams of camphor.

"	"	$212-213^{\circ}$	gave 6.1 grams of camphor.
"	"	$213-220$	" 2.0 " "
"	"	$220-230$	" only trace.

11.3 grms. of camphor = 5.6 p. c.

(b.) 100 grams of the oil (boiling at $212-213^{\circ}$) from experiment (a) was redistilled; the distillate cooled and treated in the same way gave 4.9 grams of the camphor = 4.9 per cent.

(c.) 100 grams of the compound previously freed from camphor was put in a pressure bottle and heated at 200° for 15 hours in an oil-bath; the oil cooled and the deposited camphor collected and weighed. It gave 10.2 grams of the camphor = 10.2 per cent.

(d.) 122 grams of the camphor-free oil was put in a bottle provided with a reflux condenser, and heated so that the oil was kept constantly at a gentle boil for six hours. The oil acquired a brownish colour, and the camphor produced by cooling it amounted to 13.8 grams = 11.3 per cent.

(e.) A small quantity of the pure oil was put in a bottle and heated at 100° in a water-bath for about six hours; in this case no perceptible amount of camphor was found in the oil.

These experimental results, although only approximate, tend to show that the action of heat alone upon the compound (that which was used in the above experiments being the one previously fractionated several times and freed from camphor by the aid of cold) is to polymerise a part of it with simultaneous production of camphor, the amount of which is dependent on the temperature and the time during which it is heated. During the heating of the oil, a small quantity of water was always eliminated, and this is probably due to both the conversion of the original compound into camphor and its partial polymerisation. It may also be remarked here that by spontaneously evaporating it on a watch-glass, no deposit of camphor was left, showing that camphor did not pre-exist in the compounds under examination. The composition of the substance was as follows:—

I. 0.3318 gram substance gave 0.8586 gram CO_2 and 0.3187 gram H_2O .

II. 0.2852 gram substance gave 0.7352 gram CO_2 and 0.2777 gram H_2O .

III. 0.2980 gram substance gave 0.7694 gram CO_2 and 0.2846 gram H_2O .

	I.	II.	III.	Mean.
Carbon	70.58	70.30	70.41	70.43
Hydrogen ...	10.67	10.81	10.61	10.70
Oxygen	—	—	—	18.87

100.00

	Theory for	
	$C_{10}H_{16}O_2$	$C_{10}H_{18}O_2$
Carbon.....	71.42	70.59
Hydrogen	9.53	10.59
Oxygen	19.05	18.82
	100.00	100.00

I now provisionally propose the name of "camphorogenol"* for the compound, as indicating the source from which camphor is so easily produced. It is a colourless, rather heavy oil, of a pleasant camphoraceous odour, which is, however, milder than that of camphor itself. Its sp. gr. taken at 20° is 0.9794; a preliminary determination of its rotatory power gave $[\alpha]_D = 29.6^\circ$. It is miscible in almost every proportion with alcohol, ether, or carbon bisulphide, but insoluble in water.

When camphorogenol is gently warmed with dilute nitric acid (1 acid to 20 water), it is rapidly attacked by the acid, and produces a large quantity of camphor, whilst a part of it is transformed into a yellow oil, from which further quantities of camphor can be separated on cooling. To secure the whole of the camphor thus produced, it is necessary to attach a large condensing tube to the flask in which the reaction takes place; in one experiment the amount of camphor produced was a little over 52 per cent., and it showed all the characters of an ordinary dextrorotatory camphor.

Boiling chromic acid mixture also produces the same change on camphorogenol, a large quantity of solid camphor being readily produced by the reaction.

When camphorogenol is gradually added to strong nitric acid in a flask loosely closed with a funnel at its mouth, a violent reaction sets in, with copious evolution of nitrous fumes. If the flask is heated afterwards with occasional addition of fresh acid, the compound is finally oxidised to a number of products, among which camphoric acid appears to be the main substance. It requires, however, 3 to 4 days of continued heating to effect the complete oxidation of 200 grams of camphorogenol. To obtain camphoric acid from this,

* This may otherwise be called camphor hydrate, it being represented as $(C_{10}H_{16}O, H_2O)$.

the greater part of the nitric acid is driven off, the residue diluted with water and again boiled; if any unoxidised oil or camphor be left they will pass over with the steam; on concentrating the solution, the crystals of camphoric acid separate out, and may be purified by recrystallisation from dilute alcohol. The acid is thus obtained in hard translucent needles, melting at $184-185^{\circ}$. Its apparent specific rotatory power in aqueous solution containing 3.205 grams of the substance in 100 c.c. is $[\alpha]_D = 40.3^{\circ}$, showing that camphoric acid obtained by the oxidation of camphorogenol is the ordinary dextro-rotatory form. On analysis it gave the following numbers:—

- I. 0.2683 gram substance gave 0.5885 gram CO_2 and 0.1978 gram H_2O .
 II. 0.3012 gram substance gave 0.6612 gram CO_2 and 0.2198 gram H_2O .

	I.	II.	Mean.	Camphoric acid, $\text{C}_8\text{H}_{14}(\text{COOH})_2$.
Carbon.....	59.82	59.87	59.85	60.00
Hydrogen	8.19	8.10	8.15	8.00
Oxygen	—	—	32.00	32.00
			<hr/> 100.00	<hr/> 100.00

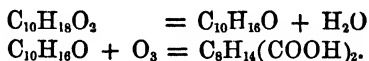
If this acid is treated with cold strong sulphuric acid in which it readily dissolves, it is deprived of the elements of a molecule of water, and on diluting the solution with water camphoric anhydride is precipitated in beautiful white flocks. This collected, washed, and dissolved in alcohol, yields the crystals of the compound in shining prisms. The numbers obtained on analysis were as follows:—

- 0.3641 gram substance gave 0.8793 gram CO_2 and 0.2559 gram H_2O .

	Found.	Camphoric anhydride, $\text{C}_{10}\text{H}_{14}\text{O}_5$.
Carbon	65.87	65.93
Hydrogen	7.90	7.69
Oxygen	26.31	26.38
	<hr/> 100.00	<hr/> 100.00

The other acids produced by the action of strong nitric acid on camphorogenol, and which can be obtained in a syrupy state by evaporating the mother-liquor after the separation of the camphoric acid, are reserved for future examination; so far as the experiments go, it appears highly probable that these oxidation products are the same as those obtained by the direct oxidation of camphor itself, for camphorogenol must be first converted into camphor before any further action can take place. The action of oxidising agents and of heat on

camphorogenol in general may be regarded as the separation of the elements of a molecule of water from the compound producing camphor, whilst at the same time the polymerisation of a part of it takes place; the production of camphoric acid from it is the result of further oxidation of the camphor formed, which, for simplicity's sake, may be written as follows:—



About 200 grams of camphorogenol were mixed with about half its weight of glacial acetic acid, the mixture put in a pressure bottle, and heated at 210° for 16 hours. After it had cooled, it was transferred to a retort and distilled; acetic acid came over first, and then an oil between 210 — 230° . This oil, which was collected in a separate receiver, deposited a good deal of camphor on cooling, and the mother-liquor on examination was found to be nothing but unchanged camphorogenol, mixed with a little of the polymeric products; but no etherified compound was obtained by this treatment.

Heating camphorogenol with benzoic acid for 20 hours at 208 — 211° gave the same negative result. The camphor produced in both cases appears to be due mainly to the action of heat, and not of acids, on the camphorogenol. These experiments tend to show that camphorogenol is not alcoholic in character.

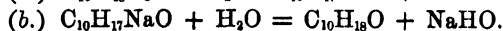
Camphorogenol was dissolved in twice its weight of absolute alcohol, and clean pieces of sodium added to it as fast as it was taken up. Application of heat to the solution was avoided, as it makes the reaction too violent, and even without it the temperature soon rises to about 90 — 100° , so that it was found necessary to provide the reaction flask with a reflux condenser to retain the alcoholic vapour which distils. Addition of sodium was continued until its action on the solution became very slow; the whole was poured into a large quantity of water, thoroughly stirred, and then neutralised with hydrochloric acid. On standing, an oily layer of peculiar odour soon separated from this solution; after some time this became pasty from deposition of crystals. This pasty oil was separated from the water, dissolved in alcohol, again acted on with sodium, the product decomposed with water, &c.; this treatment was repeated thrice, when a crystalline body was obtained, looking like borneol, but possessing a slightly different odour from that of the natural variety. The crystals were collected, pressed, and purified by repeated sublimation. On analysis it gave the following numbers:—

I. 0.4183 gram substance gave 1.1928 gram CO_2 and 0.4450 gram H_2O .

II. 0.3072 gram substance gave 0.8762 gram CO_2 and 0.3249 gram H_2O .

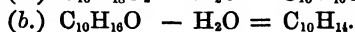
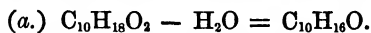
	I.	II.	Mean.	Borneol, $\text{C}_{10}\text{H}_{18}\text{O}$.
Carbon	77.80	77.78	77.79	77.92
Hydrogen	11.82	11.75	11.78	11.69
Oxygen	—	—	10.43	10.39
			<hr/> 100.00	<hr/> 100.00

The substance melts at 198° in a capillary tube, and boils at 212° . Its apparent rotatory power in alcoholic solution containing 3.090 grams substance in 100 c.c. is $[\alpha]_D = 22.9^\circ$. When heated with dilute nitric acid, it is oxidised to camphor; with zinc chloride, it readily gives a hydrocarbon possessing the same characters as borneene ($\text{C}_{10}\text{H}_{16}$), obtainable from borneol. In fact, all the properties of the compound examined show that it is chemically identical with camphol; its only peculiarities are its odour and its action on polarised light; it is likely that the value obtained for its rotatory power may really be an apparent one, and if the compound had been properly fractionated, it might have been split up into camphols of different optical activity. The production of camphol from camphorogenol may be represented in the following way:—



When camphorogenol is heated with about one-third its weight of zinc chloride, a violent reaction sets in, and almost the whole of the substance is converted into a thick tarry matter, from which nothing can be obtained by distillation with steam; if zinc chloride be gradually added to the gently heated oil, the reaction takes place but slowly, and a small quantity of camphor is thereby produced. A better result is obtained by using phosphoric anhydride, but this also requires careful heating of the mixture for rather a long time. By so doing a considerable quantity of the substance is resinised, and if the product is now steam-distilled, about one-fourth of the quantity of the substance originally taken passes over as a light oil, which has an odour resembling that of a mixture of cymene with a little camphor; fractionated over sodium, it boiled chiefly between 170 — 178° , and on oxidising it with strong chromic acid mixture, it gave terephthalic acid, showing that the hydrocarbon produced is a cymene. This reaction may be explained in two ways:—First, the production of cymene can be looked upon as the result of the direct dehydration of camphorogenol, as $\text{C}_{10}\text{H}_{18}\text{O}_2 - 2\text{H}_2\text{O} = \text{C}_{10}\text{H}_{14}$, which is, however, rather impro-

bable; secondly, the reaction may be represented as taking place in two stages, camphor being produced first, and then cymene from it:—



As far as the examination of the properties of camphorogenol goes, it may be regarded as possessing the character of a hydrate ($\text{C}_{10}\text{H}_{16}\text{O}, \text{H}_2\text{O}$), and as the elimination of the elements of a molecule of water from it can be effected by the simple action of heat, it may also be easy to conceive the possibility of such a change by means of phosphoric anhydride, camphor being then produced, and the derivation of cymene from it may be said to be more in accordance with known facts than the hypothesis first given. That camphor is really produced during the first part of the reaction is also in favour of the latter view, although this may likewise be regarded partly as the result of the action of heat alone on camphorogenol.

Summary of the results and the consideration of the possible chemical changes within the oil attending the production of camphor and during its ageing:—

(a.) The experiments recorded in the foregoing pages show that camphor oil is a complex mixture consisting of two terpene hydrocarbons with camphor and camphorogenol.

(b.) One of the lighter terpenes (b. p. = 156°) in the oil is certainly chemically identical with the terebenthene of French turpentine oil, and the other (b. p. 172 — 173°) very probably with citrene from lemon oil.

(c.) Camphor oil terebenthene has the specific rotatory power of $[\alpha]_D = -76.1^\circ$, and is therefore the most optically active of all the terebthenes; the properties of its derivatives, such as nitrosyl chloride and nitroso-compounds, the hydrochlorides, and the terpin, are all the same as those obtainable from the terebenthene of French turpentine oil.

(d.) The camphor oil citrene has the specific rotatory power of $[\alpha]_D = -68.3^\circ$; it readily gives a dihydrochloride, melting at 59° , but neither nitroso-compound nor terpin can be obtained from it by ordinary methods; its dibromide gives cymene, from which terephthalic acid can be obtained by oxidation with chromic acid liquor; by oxidising it with dilute nitric or chromic acid, no camphor is produced, but chiefly acetic, oxalic, and carbonic acids, &c.; in all these respects, as also in odour, it closely resembles the citrene from lemon oil.

(e.) Camphorogenol is the main constituent of the camphor oil. It gives camphor by the simple action of heat in presence of air, and also by treatment with oxidising agents. By secondary reactions, it

gives cymene with dehydrating agents, and camphoric acid (and also other acids) with strong nitric acid; these reactions, as also the non-production of compound ethers by heating the substance with organic acids, indicate that it is not ketonic like camphor, nor alcoholic like borneol, but belongs very probably to the class of hydrates, and its formula may be put down as $C_{10}H_{16}O, H_2O$.

(f.) Camphorogenol is very closely related to both camphor and camphol, its conversion to either of them being readily effected; to the former by oxidation, and to the latter by reduction with sodium; it is as if it were a connecting link between the two, and is the source from which camphor is produced in the oil.

Mr. Oishi has shown that a freshly distilled oil from which no camphor had separated on cooling, kept in a well-closed bottle, gradually acquires a yellow colour, and after the lapse of several months there is produced some quantity of solid camphor which can be separated by cooling the oil; the same result can also be brought about by passing a stream of oxygen gas into the oil. The constituents of the camphor oil are fairly stable when kept in a pure state, but when they exist in admixture with each other, they appear to undergo a series of changes, so that it seemed desirable to ascertain by direct experiment the effect of ageing on the oil.

I prepared an artificial mixture of camphor oil, taking its pure constituent bodies. This mixture (55 parts of camphorogenol + 30 parts of citrene + 15 parts of terebenthene) was put in a stoppered bottle with sufficient air in it, and heated in a water-bath for about 10 days, with the view of accelerating the change. The oil gradually acquired a yellow colour, and at the end of the experiment it deposited about 7 per cent. of camphor on cooling. The oil, now freed from camphor as far as practicable, was distilled with water, by which the terpenes with a little camphor passed over with the steam, whilst the greater part of the camphorogenol with some polymeric products remained in the retort. The residue in the retort (somewhat coloured), separated from the water and weighed, amounted to 58 per cent.

The terpenes alone treated in the same way gave not a trace of camphor.

Although no great accuracy can be claimed for the above experiment, yet this, taken in connection with the properties of camphorogenol before mentioned, serves, I think, to show that the production of camphor in the oil is due to the oxidation of camphorogenol, whilst a part of it is simultaneously polymerised into a dark oil, and that such a change in the character of the oil can be more quickly effected by the aid of heat in the presence of oxygen. The increase in weight of the camphorogenol after the experiment also shows that it must

have been produced from some other body or bodies, probably the terpenes.

We know that camphene, by oxidation with chromic liquor, can be changed into camphor, but we have as yet no direct means by which terebenthene or citrene can be converted into camphor, so that from this it also appears that the production of camphor within the oil cannot be by the direct oxidation of the terpenes present, but by that of camphorogenol, as before stated, this in turn being very probably produced by certain processes of oxidation from the terpenes.

According to Sobrero (*Annalen*, 1851, 80, 106), an aqueous turpentine oil kept for some time in a sunny place in an atmosphere of oxygen, deposits stellate groups of crystals on the sides of a vessel containing the oil. This substance has the composition $C_{10}H_{18}O_2$, being produced from the terpene $C_{10}H_{16}$ by the assimilation of water and oxygen.

A similar reaction may be supposed to take place within the camphor oil, and if that be so, the production of camphorogenol may be regarded as resulting from the joint hydration and oxidation of the terpenes, viz. :—



The chemistry of the camphor oil will then be a very complicated one, and the processes of hydration, oxidation, and polymerisation of the constituent bodies are simultaneously occurring changes attending the final production of camphor by the ageing of the oil.

Before closing the present note, a few words remain to be said with regard to the nature of the results obtained on the constituents of the camphor oil by other observers.

Whilst confirming the general results obtained by Becket and Wright that the portion of the oil boiling at about 170° chiefly consists of a terpene, some of the experimental conclusions arrived at by Oishi are quite at variance with the facts established in the present investigation.

Oishi obtained two compounds, $C_{12}H_{20}$ and $C_{10}H_{16}O$ (liquid isomeride of camphor), boiling respectively at $178-180^\circ$ and $180-185^\circ$. My patient endeavours to isolate these compounds from the oil have hitherto been failures, for I found that whenever such portions of the oil are fractionated until the boiling points of the substances are constant, they can finally be split up into the citrene and a small quantity of camphor. No description of the definite chemical and physical properties of the compounds, or of the nature of their decomposition products, is given by Oishi; and supported only by a single analysis of each and the determination of the vapour-density of one of them, there is, I think, scarcely satisfactory evidence of their real

existence in the oil; moreover, some of his analytical numbers appear to agree better with a mixture of the citrene and camphor than with the formula given by Oishi, thus:—

	Oishi found for $C_{12}H_{20}$.	For liquid camphor, $C_{10}H_{16}O$.	Calculated for $7(C_{10}H_{16}) +$ $C_{10}H_{16}O$.	Calculated for $8(C_{10}H_{16}O) +$ $C_{10}H_{16}$.*
Carbon ..	86.95	78.87	86.95	78.80
Hydrogen	12.29	10.73	11.59	11.59
Oxygen ..	—	10.40	1.45	9.61
	<u>99.23</u>	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>

	Theory for $C_{12}H_{20}$.	Theory for $C_{10}H_{16}O$.
Carbon	85.71	78.96
Hydrogen	14.29	10.52
Oxygen	—	10.52
	<u>100.00</u>	<u>100.00</u>

The determination of some of the more important physical constants of the constituents of the camphor oil now in progress will, I hope, throw more light on the nature of these bodies.

In conclusion, I have to return my best thanks to Professor J. Sakurai, of Tokio University, for his great kindness in aiding me in preparing the present communication.

* Such a mixture of the citrene with camphor would surely possess a much higher boiling point than 180—185°.

LXXVIII.—*On the Synthetical Formation of Closed Carbon-chains.*

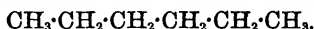
by W. H. PERKIN, Jun., Ph.D., Privatdocent at the University of Munich.

Part I. *On Some Derivatives of Trimethylene.*

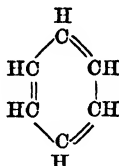
INTRODUCTION.

ORGANIC chemistry is generally divided into two distinct sections, namely, the fatty series and the aromatic series.

The members of the first series are derivatives of methane, the simplest constituted hydrocarbon, and are characterised by their open or chain form, as for example in the case of normal hexane,



Aromatic compounds are, on the contrary, derivatives of a much more complicated basis, namely of benzene, C_6H_6 , which, as was first shown by Kekulé in 1865, has the constitution



i.e., contains a ring consisting of six carbon-atoms joined together in such a way as to form a regular hexagon.

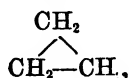
These two series differ in the most marked way from one another, the members of the aromatic series being particularly characterised by their extreme stability. Thus, whilst it is a matter of comparative ease to split up a more complicated fatty body into its simpler components, by chemical reactions, it is only with the greatest difficulty that the benzene-ring can in any way be decomposed.

In considering these great differences, one cannot but be surprised that no intermediate series should be known, the members of which would possess partly the character of fatty, and partly that of aromatic compounds.

It is not absolutely necessary that a carbon-ring should contain six carbon-atoms, as it is quite reasonable to suppose that rings constructed with 3, 4, 5, 7, &c., carbon-atoms should be capable of existing. The few experiments which have up to the present time

been tried to test this supposition, have not thrown much light on the subject.

The improbability of the existence of a three-carbon-ring



which would be isomeric with propylene, $\text{CH}_3\cdot\text{CH}:\text{CH}_2$, is the subject of a long discussion in a paper by Victor Meyer (*Annalen*, **180**, 196).

Reboul (*Compt. rend.*, 22 Juin, 1874) attempted to obtain this hydrocarbon by treating trimethylene bromide with sodium at high temperatures, and found that a gas was formed, which he supposed to be ordinary propylene. Freund (*Monatsh. Chem.*, 1882, 622), who has since very carefully studied this reaction, comes to very different conclusions. On heating trimethylene bromide, $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$, with sodium at temperatures not above the boiling point of the bromide (165°), Freund obtained a gas which when passed through bromine was only very slowly and with great difficulty attacked by it, trimethylene bromide being regenerated, whereas propylene, as is well known, is instantly absorbed by bromine, propylene bromide, $\text{CH}_3\cdot\text{CHBr}\cdot\text{CH}_2\text{Br}$ being formed.

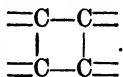
Still more curious is the fact (also observed by Freund) that this gas when passed through fuming hydriodic acid is easily absorbed, normal propyl iodide, $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\text{I}$, being produced.

Propylene, under the same circumstances, gives isopropyl iodide, $\text{CH}_3\cdot\text{CHI}\cdot\text{CH}_3$.

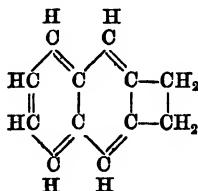
There can therefore be no doubt that this gas is not propylene; it

must therefore be trimethylene, $\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 - \text{CH}_2 \end{array}$.

No attempts appear to have been made to synthesise the corresponding four-carbon-ring,



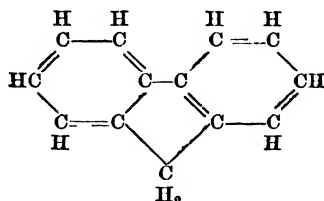
There is, however, one body in the aromatic series, namely,



acenaphthene, which without the slightest doubt contains such a ring,

and this being a very stable body, it is lawful to assume that the ring,
 $\begin{array}{c} \text{H}_2-\text{CH}_2 \\ | \\ \text{H}_2-\text{CH}_2 \end{array}$, should not be a body incapable of existence.

An example of a hydrocarbon in the aromatic series containing a
 ve-carbon-ring is *fluorene* :—



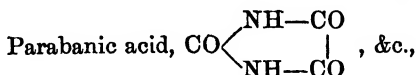
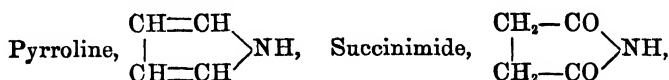
If we examine further the possibility of the existence of four- and
 ve-carbon-rings alone, we find that several bodies in the fatty
 series are already well known, which are closely allied to these

hypothetical hydrocarbons. Thus furfuran, $\begin{array}{c} \text{CH}=\text{CH} \\ | \\ \text{CH}=\text{CH} \end{array} \text{O}$, is a four-

carbon-chain, which is closed by an oxygen-atom, a fact which
 would rather tend to weaken the compound than otherwise, and
 yet this body possesses a considerable degree of stability, forcing

one to come to the conclusion that the simple ring, $\begin{array}{c} \text{CH}=\text{CH} \\ | \\ \text{CH}=\text{CH} \end{array}$ (that

is, tetrene), should certainly be capable of existence. On pursuing the
 subject further, we find such bodies as—



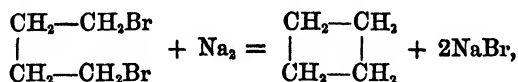
which all contain rings made up of five atoms of carbon or nitrogen,

a fact which must lead one to suppose that the ring $\begin{array}{c} \text{C}-\text{C} \\ | \\ \text{C}-\text{C} \end{array} \text{C}$ cannot

be an unstable combination. Such considerations as these made it
 appear interesting to pursue the subject further, and if possible either
 to fill up the gaps by synthesising the missing rings, or if that were
 not possible, at all events, to give some plausible reason why they
 should not be capable of existence.

In order to synthesise the four-carbon-ring, the first idea that would

naturally occur would be to prepare a dibromide of the formula $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$, and then treat this with sodium,

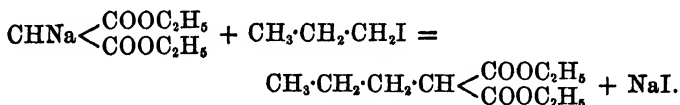


a reaction exactly similar to that by which Freund obtained trimethylene from trimethylene bromide, $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$, and sodium.

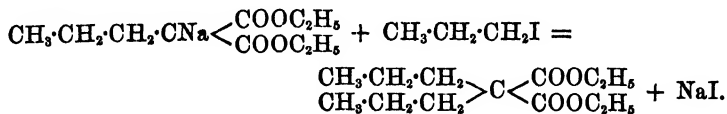
There is, however, curiously enough, no reaction in the fatty series by which dibromides can be prepared having the two bromine-atoms situated at opposite ends of the carbon-chain; after a long series of experiments, no practicable method could be found for producing such compounds in sufficient quantities for further experiments.

Another method for forming these ring-compounds was, however, afterwards found, which did away in the meanwhile with the necessity of using bromides with longer chains than trimethylene bromide.

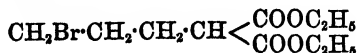
It is a well-known fact that if ethyl malonate is mixed with sodic ethylate, it forms a sodium compound, which when treated with the halogen-derivatives of the alcohol radicals gives the higher homologues of ethyl malonate; thus on treating it with propyl iodide, ethyl propylmalonate is formed—



This ethyl propylmalonate again is itself capable of forming a sodium compound, which on further treatment with propyl iodide gives ethyl dipropylmalonate thus :—

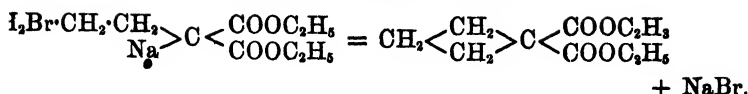


Now if it were possible to brominate ethyl propylmalonate in such a way that the bromine would attack the methyl-group, and that group alone, the compound

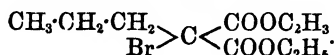


would be obtained, which when treated with sodic ethylate would form a sodium compound; this on heating should be decomposed in the following way :—

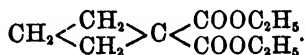
“



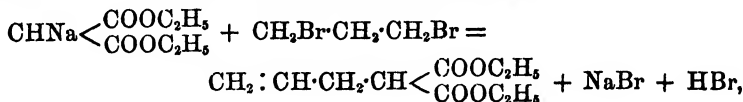
is unfortunately a most difficult matter to prepare a brominated compound such as that represented above, and all experiments which are tried for this purpose failed. The bromine always enters the molecule in the CH group, forming a compound of the formula—



this difficulty can, however, be got over, if one starts in the first place with a dibromide which already contains the two bromine atoms in the right position, and such a bromide is trimethylene bromide, $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$. If the sodium compound of ethyl malonate is treated with trimethylene bromide an ethereal salt is obtained, which, from the experiments already made, must without doubt contain a four-carbon-ring and have the following constitution:—



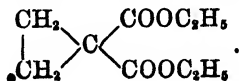
The proofs that this compound has this constitution are the following: If the action of trimethylene bromide on ethyl malonate is studied, it is seen that there are only two possible ways in which the reaction can take place—I. That a body possessing the above constitution is formed. II. Or that the reaction is the following:—



i.e., that ethyl allylmalonate is formed.

That this is not the case I shall be able to show decisively when the substance in question is treated of in Part II of this paper. One is therefore forced to come to the conclusion that a derivative of a closed chain containing four carbon-atoms has been formed. This reaction is, moreover, not confined to trimethylene bromide. Ethylene bromide acts on ethyl malonate in exactly the same way, producing compounds which are perfectly analogous to those obtained by the action of trimethylene bromide.

Thus the first product of the action of ethylene bromide on ethyl malonate is a three-ring-derivative, having the formula—

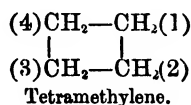
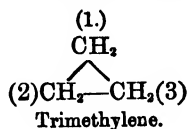


It was now necessary to find some suitable form of *nomenclature* for these bodies, and after some consideration it was thought that the simplest method would be to regard the saturated hydrocarbons themselves as multiples of methylene, CH_2 , and thus name them di-, tri-, tetra-, penta-, &c., methylene, as is easiest seen from the following table:—

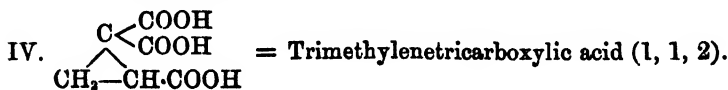
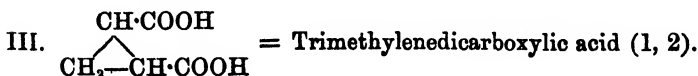
$=\text{CH}_2$	$\begin{array}{c} \text{CH}_2 \\ \\ \text{CH}_2 \end{array}$	$\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_1 - \text{CH}_2 \end{array}$	$\begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ \quad \\ \text{CH}_2 - \text{CH}_2 \end{array}$	$\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \quad \text{CH}_2 \\ \quad \\ \text{CH}_2 - \text{CH}_2 \end{array}$	$\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \quad \text{CH}_2 \\ \quad \\ \text{CH}_2 \quad \text{CH}_2 \\ \\ \text{CH}_2 \end{array}$
Methylene.	Di- methylene (Ethylene)	Tri- methylene	Tetra- methylene	Penta- methylene	Hexa- methylene

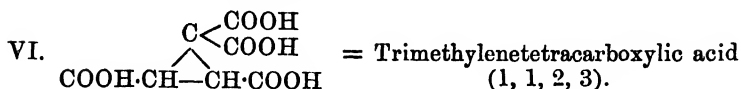
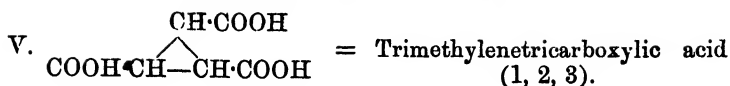
This is not only very clear and easy to understand, but is also of general application to all hydrocarbons which are built up of CH_2 groups.

Another question is how to distinguish the different possible isomeric derivatives of such hydrocarbons from each other, and I think that in order to meet this difficulty in the clearest and most satisfactory manner, it will be best to number the different carbon-atoms in the ring as proposed by Baeyer (*Ber.*, 17, 960); thus:—

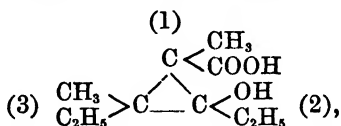


The necessity for some such system of nomenclature will be seen directly on examining the following table of the carboxylic acids of trimethylene, which have all been obtained:—





All other derivatives of such closed chains can be formulated in an exactly similar way, and thus directly recognised and identified by the name. Thus a compound of the following complicated structure—



would be dimethyldiethylhydroxytrimethylenecarboxylic acid (1, 3, 2, 3, 2, 1).

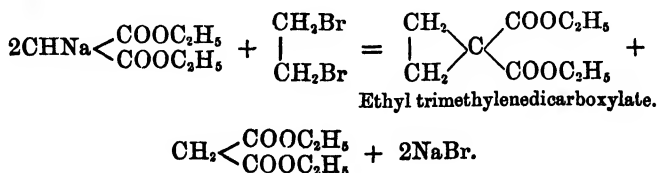
Part I of this paper, I have devoted entirely to the derivatives of trimethylene. In Part II I hope to have the honour of bringing an account of some tetramethylene-derivatives before the Society.

Before entering into the details of this research, I must express my sincerest thanks to Professor Adolf Beyer, in whose laboratory the experiments were carried out, for the great interest which he always took in the work, and for his valuable help in overcoming all difficulties, and also to Herr Carl Bernhart for his assistance in the experimental part.

ACTION OF ETHYLENE BROMIDE ON ETHYL MALONATE.

Ethyl Trimethylenedicarboxylate (1, 1).

If the sodium compound of ethyl malonate is digested with ethylene bromide for some hours, sodic bromide is precipitated and the ethyl salt of trimethylenedicarboxylic acid (1, 1) is formed according to the following equation:—



In carrying out this synthesis, the following method, which I give

in full, has, after a great many experiments, been found to give the best results.

10 grams of sodium are dissolved in 100 to 120 grams of absolute alcohol, and, after cooling well, a mixture of 70 grams of ethyl malonate and 42 grams of ethylene bromide are slowly poured in, care being taken that the mixture does not get hot. The milky liquid is then transferred to a soda-water bottle and heated in a water-bath for six hours at 100° , by which means the sodium compound is completely decomposed. The end of the reaction can easily be determined by taking out a small portion, diluting it with water, and testing with litmus-paper, when the liquid should have a neutral reaction.

In preparing this compound, it has been found convenient to work with five such portions, that is, with 350 grams of ethyl malonate. As soon as the reaction is completed the contents of the five bottles are mixed with twice the bulk of water and extracted three or four times with ether. The ethereal solution is then well washed with water, dried over calcic chloride, and the ether distilled off, when 385 grams of an almost colourless oil remain behind; on distilling this, it gives the following fractions:—

120— 180°	=	16 grams.
180— 225°	=	330 „
Residue in retort	=	13 „

The fraction 180— 225° , which contains all the ethyl trimethylene-dicarboxylate, as well as the unchanged ethyl malonate, is next mixed with 70 grams of ethylene bromide, a solution of 17 grams of sodium in 180 to 200 grams of absolute alcohol is poured in, and the whole is again heated in soda-water bottles for six hours, by which means a great part of the ethyl malonate is transformed into ethyl trimethylene-carboxylate. Water is then added, and the product extracted with ether and treated exactly as described before. On distilling off the ether, 325 grams of oil remain behind, which on fractioning give the following results:—

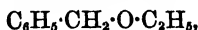
120— 180°	=	24 grams.
180— 225°	=	275 „
Residue	=	12 „

The fraction 180— 225° still contains a considerable quantity of unchanged ethyl malonate which is removed by treating it with sodic ethylate and benzyl chloride. By this means all the ethyl malonate present is transformed into ethyl benzylmalonate boiling at 300° , which can easily be separated by fractional distillation. This fraction, 180— 225° , is therefore mixed with 120 grams of benzyl chloride, and the whole heated with 20 grams of sodium dissolved in

220 grams of absolute alcohol for two hours, at the end of which time the reaction is finished. After adding water and extracting with ether, 355 grams of oil are obtained which, on distillation, give the following fractions :—

120—170° =	4 grams.
170—260 =	202 „
Residue =	132 „

The fraction 170—260° contains all the ethyl trimethylenedicarboxylate, together with a certain quantity of benzyl ether,



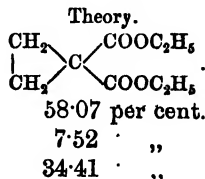
produced by the action of benzyl chloride on any excess of sodic ethylate. This can, however, be almost entirely removed by oft-repeated careful fractioning either with a column or with a Würtz flask with a long neck (30—40 cm.). In this way, 100 to 120 grams of nearly pure ethyl trimethylenedicarboxylate are obtained boiling at 208—210° (at 720 mm.).

Should this ether when tested be found to contain chlorine (due to traces of undecomposed benzyl chloride), it is mixed with its own volume of glacial acetic acid and warmed on a water-bath with a little zinc-dust. After diluting with water, the product is extracted several times with ether, the ethereal solution well washed with water and dilute sodic carbonate solution, and dried over potassic carbonate. After removing the ether, the residual oil is again purified by fractioning.

This substance gave the following numbers on analysis :—

- I. 0.2064 gram substance gave 0.1453 gram H_2O and 0.4364 gram CO_2 .
 II. 0.2018 gram substance gave 0.1420 gram H_2O and 0.4284 gram CO_2 .
 III. 0.1977 gram substance gave 0.1320 gram H_2O and 0.4201 gram CO_2 .

	Found.			Theory.
	I.	II.	III.	
C...	57.66	57.90	57.95 per cent.	58.07 per cent.
H...	7.82	7.81	7.42 „	7.52 „
O...	34.52	34.29	34.63 „	34.41 „



The vapour-density determined in aniline vapour by Hofmann's method gave—

$$D = 6.32^\circ. \text{ Theory, } \text{C}_8\text{H}_{14}\text{O}_4, D = 6.43^\circ.$$

The substance is therefore ethyl trimethylenedicarboxylate. It is a colourless, pleasant-smelling oil which boils at 210° (720 mm., 213° at 760 mm.). Its density is:—

$$d_{15^{\circ}}^{15^{\circ}} = 1.06463. \quad d_{25^{\circ}}^{25^{\circ}} = 1.05664.$$

The boiling point, 206 – 208° , which I first gave in a short notice in the *Berichte* (17, 55), is slightly too low.

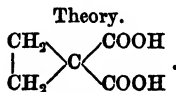
Trimethylenedicarboxylic Acid (1, 1).

In order to obtain this acid, pure ethyl trimethylenedicarboxylate was dissolved in a little alcohol and a slight excess of strong alcoholic potash slowly poured in. As soon as the violence of the reaction had subsided, the whole was heated in a flask connected with a reflux condenser for about four hours on a water-bath, by which means the ether was easily saponified. Water was then added, the whole heated on a water-bath until the alcohol had been driven off, and the residue filtered. The filtrate was then acidified with dilute sulphuric acid and repeatedly extracted with pure ether, until a drop of the ethereal solution on evaporation on a watch-glass left only a very slight residue. The ethereal solution was then dried over calcic chloride and the bulk of the ether distilled off. The concentrated ethereal solution, on evaporation, deposited an almost colourless semi-solid acid, which solidified almost entirely after standing for some hours over sulphuric acid in a vacuum. In order to remove a small quantity of mother-liquor, the crystals were spread out on a porous plate, by which means they were obtained almost colourless. They were further purified by recrystallisation from chloroform or ether, and then analysed with the following result:—

I. 0.1983 gram substance gave 0.0870 gram H_2O and 0.3335 gram CO_2 .

II. 0.1920 gram substance gave 0.0813 gram H_2O and 0.3212 gram CO_2 .

	Found.		Theory.
	I.	II.	
C	45.87	45.63 per cent.	46.15
H	4.87	4.76 „	4.62
O	49.26	49.61 „	49.23



This substance is therefore trimethylenedicarboxylic acid (1, 1). It melts at 140 – 141° , and at 160° begins to decompose slowly, much more rapidly at 200° , carbonic anhydride being driven off. It is easily soluble in water, much more so than in ether, and can be

recrystallised from this solvent by allowing the concentrated solution to stand over sulphuric acid in a vacuum.

It is thus obtained in beautiful colourless prisms, which, however, contain water of crystallisation. Trimethylenedicarboxylic acid is only extremely slowly oxidised by potassic permanganate in alkaline solution, and it is but little affected by warming with chromic acid and dilute sulphuric acid. The acid is best purified by allowing the concentrated ethereal solution to evaporate slowly, when beautiful colourless prisms are formed. Professor Haushofer was kind enough to measure them for me, with the following results:—

Crystalline System; Triclinic.

$$\alpha = 88^\circ 20'$$

$$\beta = 92^\circ 40'$$

$$\gamma = 92^\circ 38'$$

$$a : b : c = 0.7712 : 1 : 0.8702.$$




Apparently rectangular prismatic crystals, with the combinations, $\infty P \infty$ (*a*), $\infty P \infty$ (*b*), $o P$ (*c*), ∞P_1 (*p*), $P_1 \infty$ (*r*), $\frac{1}{2} P_1 \infty$ (*s*). Usually, *r* is in the direction of the vertical axis. The faces, with the exception of *b* and *p*, not well developed. The face *s* was only observed in one crystal. The cleavage is perfect in the direction *r*, the cleavage surface is fibrous as in gypsum in the direction *P*.

	Observed.	Calculated.
$c : a =$	$92^\circ 36'$	—
$a : b =$	$92^\circ 34'$	—
$c : b =$	$88^\circ 48'$	—
$b : p =$	$129^\circ 14'$	—
$r : a =$	$137^\circ 33'$	—
$s : a =$	$118^\circ 00'$	$118^\circ 47'$
$r : p =$	$126^\circ 47'$	$126^\circ 59'$

The solution of this acid in chloroform is not affected by bromine at ordinary temperatures, and only very slowly on warming, hydro-

bromic acid being evolved. Neither is it affected by treating it with sodium amalgam, even after remaining in contact with it for some days.

In order to characterise this acid better, the following salts were next examined.

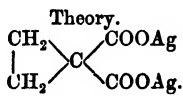
Ammonium Salt.—This salt is easily prepared by neutralising the aqueous solution of the free acid with ammonia. On allowing the solution to evaporate over sulphuric acid in a vacuum, the salt crystallises out in beautiful four-sided plates , which give a fine play of colours under the influence of polarised light.

Silver Salt.—If nitrate of silver is added to a solution of the ammonium salt, the silver salt is precipitated as a white voluminous mass, almost insoluble in cold water. It dissolves, although with difficulty, in hot water, and separates out on cooling as a white powder, which on examination with a microscope is seen to consist of a mass of small needles.

For analysis, the salt was dried over sulphuric acid in a vacuum.

- I. 0.2440 gram substance gave 0.0273 gram H_2O , 0.1516 gram CO_2 , and 0.1539 gram Ag.
 II. 0.3054 gram substance gave 0.0314 gram H_2O , 0.1892 gram CO_2 , and 0.1920 gram Ag.

	Found.		Theory.
	I.	II.	
C	16.95	16.89	per cent. 17.44 per cent.
H	1.24	1.14	1.16 "
Ag....	63.07	62.87	62.79 "
O	18.74	19.10	18.61 "



Copper Salt.—If a solution of cupric sulphate is added to the ammonium salt, a beautiful deep blue solution is obtained, but no precipitate is formed. On boiling, however, or on partial evaporation, the copper salt crystallises out in a mass of magnificent deep blue crystals, which when seen under the microscope have the following forms.



The salt was collected, well washed with hot water, in which it is sparingly soluble, and dried over sulphuric acid in a vacuum. It then contains 1 mol. H_2O , which, however, cannot be directly determined, as the whole is not driven off below $170-180^\circ$, and at that temperature the salt undergoes slight decomposition.

I. 0.3543 gram substance gave 0.1318 gram CuO .

II. 0.3432 ,, ,, 0.1330 ,,

Found.		Theory.
I.	II.	
Cu....	29.70 30.93	$\begin{array}{c} \text{CH}_2 \\ \\ \text{CH}_2 \end{array} \text{C} \begin{array}{l} \diagup \text{COO} \\ \diagdown \text{COO} \end{array} \text{Cu} + \text{H}_2\text{O}.$
		30.24

When heated to 160° , this beautiful deep blue salt is transformed into a light green powder.

Barium Salt.—This salt was prepared by adding a solution of barium chloride to the ammonium salt, when it is obtained as a heavy white precipitate, which under the microscope is seen to consist of a mass of fine crystals. This salt is free from water of crystallisation. Analysis gave the following numbers:—

0.2695 gram substance gave 0.2350 gram BaSO_4 .

	Found.	Theory. $\text{C}_6\text{H}_4\text{BaO}_4$.
Ba.....	51.27 per cent.	51.69

Lead Salt.—This salt is precipitated on adding lead acetate to a solution of the ammonium salt as a heavy white amorphous mass, practically insoluble in cold water. In hot water it is slightly soluble, and separates out on cooling in an amorphous condition. It appears to contain no water of crystallisation. For analysis, the salt was dried at 100° .

I. 0.3028 gram substance gave 0.2716 gram PbSO_4 .

II. 0.2381 ,, ,, 0.2154 ,,

Found.		Theory.
I.	II.	
Pb....	61.28 61.46	$\begin{array}{c} \text{CH}_2 \\ \\ \text{CH}_2 \end{array} \text{C} \begin{array}{l} \diagup \text{COO} \\ \diagdown \text{COO} \end{array} \text{Pb}.$
		61.79 per cent.

Besides the above-mentioned salts, two others have been examined by Roeder (*Annalen*, **227**, 16), namely:—

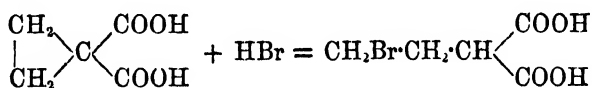
The *acid barium salt*, $(\text{C}_6\text{H}_5\text{O}_4)_2\text{Ba} + 4\text{H}_2\text{O}$, which crystallises from water in prismatic crystals.

The *acid silver salt*, $\text{C}_6\text{H}_5\text{O}_4\text{Ag}$, which crystallises from water in long colourless needles.

ACTION OF HYDROBROMIC ACID ON TRIMETHYLENEDICARBOXYLIC ACID.

γ-Bromethylmalonic Acid.

It has already been mentioned that trimethylenedicarboxylic acid is not only unaffected by nascent hydrogen, but that its solution in chloroform can be left for a long time in contact with bromine, without any appreciable change taking place. As soon, however, as it is treated with hydrobromic acid (sp. gr. 1·83), it undergoes a remarkable change, taking up the elements of HBr, and being instantly converted into bromethylmalonic acid according to the equation—

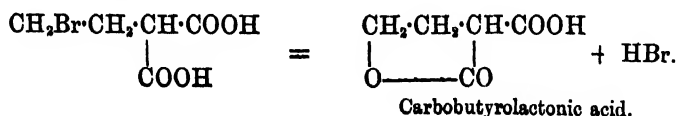


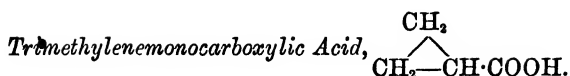
This decomposition was first noticed by Fittig and Roeder (*Ber.*, **16**, 2592), but as it was of considerable importance I repeated the experiment, and found their observations to be correct. If trimethylenedicarboxylic acid is mixed in a test tube with a concentrated solution of hydrobromic acid (sp. gr. 1·83) it dissolves, forming a clear solution, which, however, on shaking, or if the sides of the vessel be scratched with a glass rod, begins to deposit crystals, the crystallisation going on till the whole becomes solid. The crystals are next roughly separated from the mother-liquor by spreading the mass out on a porous plate and then drying it over sulphuric acid in a vacuum. It is easily obtained pure by one crystallisation from chloroform. Analysis:—

0·3313 gram substance gave 0·2941 gram AgBr.

	Found.	Theory. $\text{C}_4\text{H}_7\text{BrO}_4$.	(Fittig and Roeder).
Br....	37·78 per cent.	37·91 per cent.	37·79 per cent.

This acid melts at 116—117°. Its constitution is further proved by its transformation into carbobutyrolactonic acid by boiling with water. (Fittig-Roeder, *loc. cit.*)





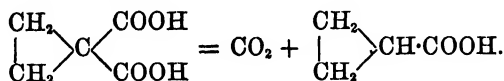
If trimethylenedicarboxylic acid is heated in an oil-bath at 210° , large quantities of carbonic anhydride are given off, and a colourless acid-smelling oil distils over, leaving a considerable residue in the retort; this, however, can be driven over by raising the temperature of the bath at the last to 250° . The distillate is next roughly purified by dissolving it in sodic carbonate solution, heating for some time in a water-bath with animal charcoal, and filtering; the filtrate is then acidified with dilute sulphuric acid, when an oily acid is precipitated, which is extracted once or twice with pure ether. The ethereal solution, after drying over calcic chloride and distilling off the ether, deposits a colourless oil, which distils almost completely between 180° and 195° .

This was further purified by repeated fractional distillation, and at last obtained pure as a colourless oil boiling constantly between 182° and 184° .* This fraction gave the following numbers on analysis:—

- I. 0.1653 gram substance gave 0.1076 gram H_2O and 0.3373 gram CO_2 .
 II. 0.1843 gram substance gave 0.1221 gram H_2O and 0.3750 gram CO_2 .

	Found.			Theory.
	I.	II.		$\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 - \text{CH} \cdot \text{COOH} \end{array}$
C...	55.67	55.49	per cent.	55.81 per cent.
H...	7.23	7.36	"	6.98 "
O...	37.10	37.15	"	37.21 "

The substance is therefore trimethylenemonocarboxylic acid, and is formed from the dicarboxylic acid according to the equation—



When cooled in a freezing mixture it solidifies to a white crystalline mass, which, however, melts again at the ordinary temperature.† This acid has the same formula as the three crotonic acids, but in all its properties, both physical and chemical, it is entirely different from them.

* Not $188-190^\circ$, which was first given in the *Berichte* (17, 57).

† Roeder (*Annalen*, 227, 25) gives the melting point of this acid as $18-19^\circ$, and the boiling point $180-181^\circ$.

α -Crotonic acid, $\text{CH}_3\cdot\text{CH}:\text{CH}\cdot\text{COOH}$, boils at $180\text{--}181^\circ$, and melts at 72° .

β -Crotonic acid, $\text{CH}_3:\text{CH}\cdot\text{CH}_2\cdot\text{COOH}$, boils at $171\cdot9^\circ$, and does not solidify at -15° .

Methacrylic acid, $\text{CH}_2:\text{C}(\text{CH}_3)\cdot\text{COOH}$, boils at $160\cdot5^\circ$, and melts at 16° .

These acids differ most from trimethylenecarboxylic acid in their behaviour towards bromine. The three crotonic acids, being unsaturated acids combine directly with 1 mol. of bromine. Trimethylenedicarboxylic acid, on the contrary, is not affected by bromine at ordinary temperatures, and only very slowly on warming, hydrobromic acid being evolved even when a large excess of the acid is present.

Trimethylenemonocarboxylic acid is partly soluble in water, forming a strongly acid solution. It has a powerful odour, recalling somewhat that of butyric acid, and a burning taste. It is heavier than water.

The ammonium salt was obtained by dissolving the acid in ammonia, and then allowing the solution to stand over sulphuric acid in a vacuum until all excess of ammonia had evaporated. On adding nitrate of silver to this solution, the silver salt is precipitated as a white voluminous mass sparingly soluble in cold water. After well washing with water and drying over sulphuric acid in a vacuum, it gave the following analytical results:—

0.2030 gram substance gave 0.0497 gram H_2O and 0.1838 gram CO_2 .

	Found.	Theory.	$\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2-\text{CH}-\text{COOAg.} \end{array}$
C...	24.69 per cent.		24.87 per cent.
H...	2.72 "		2.59 "
Ag..	55.83 "		55.96 "
O...	16.76 "		16.58 "

The silver salt dissolves sparingly in hot water, and crystallises out in small needles, on cooling.

On distilling the dry salt, a low-boiling oil is given off which appears to be the anhydride of the acid.

The calcium salt, $(\text{C}_4\text{H}_5\text{O}_2)_2\text{Ca} + 6\text{H}_2\text{O}$, and the barium salt, $(\text{C}_4\text{H}_5\text{O}_2)_2\text{Ba} + 2\text{H}_2\text{O}$, have been examined and analysed by Roeder (*loc. cit.*). They are both very easily soluble in water, and crystallise in colourless needles on evaporating their solutions.



In order to obtain this, the silver salt of the pure acid was digested with a slight excess of ethyl iodide and a little pure ether for two hours on a water-bath; in this way, the salt was easily decomposed, iodide of silver being precipitated; this was separated by filtration, and washed once or twice with small quantities of pure ether. The filtrate was then carefully distilled, particularly at first, so that none of the ethereal salt, which is very volatile, should be mechanically carried over with the ether. As soon as all the ether had distilled over, the thermometer rose rapidly to 125° , between which temperature and 140° almost all went over. This portion was then repeatedly refractioned until an oil was obtained which distilled constantly between 133° and 134° , and gave the following numbers on analysis:—

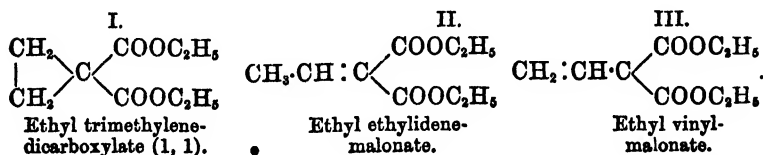
0.1232 gram substance gave 0.0988 gram H_2O and 0.2853 gram CO_2 .

	Found.	Theory.
		$\begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 - \text{CH} \cdot \text{COOC}_2\text{H}_5 \end{array}$
C.....	63.16 per cent.	63.16 per cent.
H	8.91 ,,	8.77 ,,
O.....	27.93 ,,	28.07 ,,

The substance was therefore ethyl trimethylenecarboxylate. It is a volatile oil of pleasant ethereal odour. It is not affected by treatment with bromine at ordinary temperatures, and curiously enough only very slowly so when boiled with it, hydrobromic acid being given off.

Theoretical Considerations.

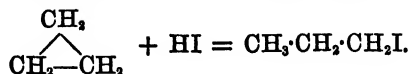
In the foregoing paper it has been taken for granted that the substances produced by the action of ethylene bromide on ethyl malonate are trimethylene-derivatives. This does not, however, necessarily follow, as there are three kinds of compounds which could be formed by this reaction, namely—



It would be very strange if a substance having the constitution expressed in formula II were formed, as this would involve an intermolecular change from $\text{—CH}\cdot\text{CH}\cdot\text{CH}_2$ to $\text{—C}\cdot\text{CH}\cdot\text{CH}_2$. The ethyl ethylidenemalonate has moreover been fully examined by Komnenos (*Annalen*, 218, 145), and in comparing this with ethyl trimethylenedicarboxylate it is easy to see that the two substances are entirely different. On heating with alcoholic potash, ethyl ethylidenemalonate is entirely decomposed into its constituents, aldehyde and malonic acid, whereas ethyl trimethylenedicarboxylate on hydrolysis gives the corresponding acid, as has been shown in this paper. That ethyl trimethylenedicarboxylate is not merely ethyl vinylmalonate (formula III) is much more difficult to prove, as it is not possible, by treating ethyl malonate with vinyl bromide, to obtain ethyl vinylmalonate synthetically, and thus enable a direct comparison to be made. As ethyl vinylmalonate is unsaturated, it would be expected to give a bromide when treated with bromine at ordinary temperatures, but this is not the case. Further, it should give on distillation an acid of the formula $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{COOH}$, which ought to be identical with one of the three known crotonic acids.

Trimethylenem monocarbonic acid, however, possesses properties entirely different from any of these acids. This difference is shown most decidedly in their behaviour towards bromine. The crotonic acids being unsaturated acids take up with the greatest ease 1 mol. of bromine, but trimethylenecarboxylic acid may be left for hours in contact with bromine without any appreciable change. All these considerations tend therefore to show that trimethylenedicarboxylic acid cannot have the constitution of vinylmalonic acid.

The readiness with which trimethylenedicarboxylic acid combines with hydrobromic acid, forming bromethylmalonic acid, appears at first sight strange, but when it is considered that trimethylene itself undergoes a decomposition exactly similar, the difficulty disappears. Freund (*Monatsh. Chem.*, 1882, 625) states that when trimethylene is made to pass through highly concentrated hydriodic acid, the ring is split, and normal propyl iodide is formed according to the equation—

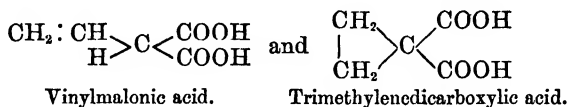


Fittig and Roeder (*loc. cit.*) noticed, however, other decompositions of this acid which are difficult to explain on the assumption of the existence of a trimethylene-ring in it. Trimethylenedicarboxylic acid is decomposed on warming with dilute sulphuric acid into the isomeric carbobutylolactonic acid, $\begin{array}{c} \text{CH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{COOH} \\ | \qquad \qquad | \\ \text{O} \text{—} \text{CO} \end{array}$, and what is

still more strange is the fact that this same trimethylenedicarboxylic acid on simple distillation (as Fittig has shown) gives as much as

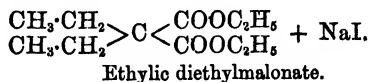
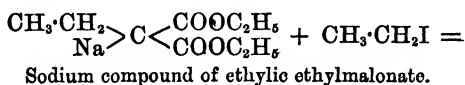
30 per cent. of butyrolactone, $\begin{array}{c} \text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2 \\ | \quad \quad | \\ \text{O} \text{-----} \text{CO} \end{array}$

These reactions are easy to explain, on the assumption that the acid is a vinylmalonic acid, such unsaturated acids having a strong tendency to undergo molecular change, and form the isomeric lactones. Otherwise it is necessary to suppose that in all these reactions the trimethylene-ring is first split, as in the above-mentioned case, with hydrobromic acid. If, however, the two formulæ are examined—

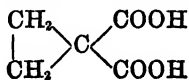


more closely, it is directly apparent that vinylmalonic acid is nothing more than a mono-substituted malonic acid corresponding with ethylmalonic acid, $\begin{array}{c} \text{CH}_3\cdot\text{CH}_2 \\ \quad \quad \quad \text{H} \end{array} > \text{C} < \begin{array}{c} \text{COOH} \\ \text{COOH} \end{array}$, whereas trimethylenedicarboxylic acid is a di-substituted malonic acid corresponding with dimethylmalonic acid, $\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array} > \text{C} < \begin{array}{c} \text{COOH} \\ \text{COOH} \end{array}$.

Now it is well known from the beautiful researches of Conrad and Bischoff, that on treating mono-substituted malonic ethers with sodic ethylate, they form sodium compounds which, when further treated with the iodides of the alcohol radicals, benzyl chloride, &c., give di-substituted malonic ethers, thus:—



It is therefore clear that if the trimethylenedicarboxylic acid be a vinylmalonic acid, that its ether when treated with sodic ethylate and benzyl chloride (for instance) would give benzylvinylmalonic acid, $\begin{array}{c} \text{C}_6\text{H}_5\cdot\text{CH}_2 \\ \text{CH}_2:\text{CH} \end{array} > \text{C} < \begin{array}{c} \text{COOH} \\ \text{COOH} \end{array}$. Should the ether, on the contrary, remain unacted on, this would be the best proof that the acid is a disubstituted malonic acid—that is, really has the constitution—



For the purpose of testing this, 77 grams of ethyl trimethylene-carboxylate were mixed with 50 grams of benzyl chloride, and a solution of 9 grams of sodium in 100 grams of absolute alcohol slowly poured in, the whole being well cooled during the operation. The mixture was then heated on a water-bath in a flask connected with a reflux condenser. The reaction set in directly, and was finished as soon as a sample, when mixed with water, was neutral to test-paper.

The product was then diluted with water and several times extracted with ether. The ethereal solution after drying over calcic chloride and evaporating, deposited 120 grams of a slightly yellowish-coloured oil which on distillation gave the following fractions:—

Under 180°..... = 7 grams.

From 180° to 220°..... = 95 „

Residue left in the re-
tort above 220°..... = 7 „

The residue above 220° was then transferred to a small retort, first roughly distilled over and then fractioned. Almost all went over below 220°, leaving a trace of a dark-brown oil behind which was too small for further examination.

The fractions below 220° were mixed and saponified by boiling with a slight excess of alcoholic potash for about four hours. On adding water a quantity of oil was precipitated which was extracted with ether and fractioned; the whole distilled over between 180 and 190°, and was found to consist of almost pure benzyl ether, $C_6H_5 \cdot CH_2 \cdot O \cdot C_2H_5$. This fraction weighed 49 grams, which, allowing for loss during fractioning, &c., is almost equivalent to the amount (54 grams) which should have been produced had the whole of the benzyl chloride used in the above experiment reacted with the sodic ethylate, and its presence in such quantity is the best proof that the ethyl trimethylenedicarboxylate had not been affected.

The solution of the potash salts produced by the hydrolysis were then evaporated on a water-bath to drive off alcohol and ether, acidulated with dilute sulphuric acid, and extracted several times with pure ether. The ethereal solution was carefully dried over calcic chloride, filtered, and the ether distilled off, when a quantity of a beautifully crystalline acid remained; this after recrystallisation from ether melted at 140° and possessed all the properties of trimethylenedicarboxylic acid. In order to be certain, a part was converted into the silver salt and analysed with the following result:—

0.2107 gram substance gave 0.1316 gram silver.

Found.
Ag.... 62.45 per cent.

Theory. $C_6H_4O_4Ag_2$.
62.79 per cent.

The acid, therefore, had been quite unacted on by the benzyl chloride.

In order to confirm this, a second experiment was made with perfectly pure ethyl trimethylenedicarboxylate which had been prepared by treating the silver salt of the pure acid with ethyl iodide. This time, 15 grams of the pure ether were treated with a large excess of sodic ethylate and benzyl chloride (namely, 4 grams Na and 20 grams benzyl chloride) in the manner described above. On fractioning the product, it all distilled over below 215° , leaving a mere trace of residue which could not be driven over without superheating the vapour and thus causing the thermometer to rise. The distillate was then saponified, but, as in the previous case, nothing but trimethylenedicarboxylic acid was obtained; no trace of a benzyl-derivative had been formed. In order to be still more certain, a large quantity of high-boiling residues, produced in purifying crude ethyl trimethylenedicarboxylate, as described at the beginning of this paper, were also examined, as it seemed likely that if any benzylvinylmalonic acid had been produced that it would probably be present in considerable quantity in these oils.

They were first distilled under diminished pressure (50 mm.) and then saponified. In this way a large quantity of a beautifully crystalline product was obtained consisting mostly of benzylmalonic acid. Traces of another acid were also present which on analysis proved to be dibenzylmalonic acid. As I have not been able to find a description of this acid, I give a short account of its properties. Dibenzylmalonic acid is sparingly soluble in cold water, more easily so in hot, and crystallises, on cooling slowly, in thick prisms; on rapid cooling, it is precipitated in fine colourless needles.

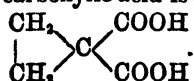
The analysis gave the following numbers:—

0.1011 gram substance gave 0.2653 gram CO_2 and 0.0545 gram H_2O .

	Found.	Theory.	$\text{C}_7\text{H}_7 > \text{C} < \begin{matrix} \text{COOH} \\ \text{COOH} \end{matrix}$
C	71.56 per cent.	71.83 per cent.	
H	5.99 ,,	5.63 ,,	
O	22.45 ,,	22.54 ,,	

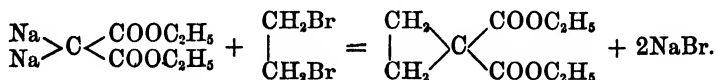
Dibenzylmalonic acid melts at $170\text{--}172^{\circ}$, and is decomposed at a higher temperature into carbonic anhydride and a solid acid, probably dibenzylacetic acid.

No trace of any other acid besides this and benzylmalonic acid could be found. There is, therefore, no doubt that trimethylenedicarboxylic acid is a di-substituted malonic acid, and has the constitution



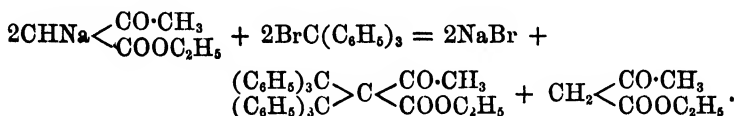
Ethyl trimethylenedicarboxylate is produced by the action of

ethyl bromide on the *mono*-sodium compound of ethyl malonate, according to the equation given on p. 817, and not on a *di*-sodium compound, as might be expected, thus:—



This is proved by the fact that large quantities of ethyl malonate always remain unchanged in this reaction, which would not be the case if the above equation were correct.

The fact that di-substituted acetoacetic ethers are formed from the *mono*-sodium compound of the latter has often been noticed. Allen and Kölliker (*Annalen*, **227**, 113) found that when perfectly pure ethyl sodacetoacetate was treated with triphenylmethane bromide, that a di-substituted derivative was formed and half the ethyl acetoacetate regenerated according to the equation—

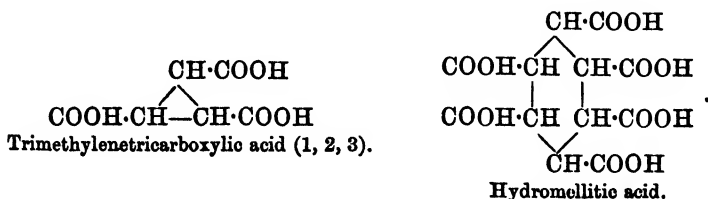


Similar results were obtained by Emil Fischer and Hermann Koch (*Ber.*, **16**, 651) on treating ethyl sodacetoacetate with phthalyl chloride, and also by Wislicenus who followed up this reaction, using ethyl malonate in place of ethyl acetoacetate.

ACTION OF ETHYL DIBROMOSUCCINATE ON ETHYL MALONATE.

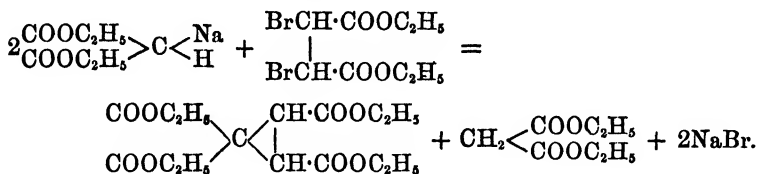
Ethyl Trimethylenetetracarboxylate (1, 1, 2, 3).

In order to get further knowledge as to the properties of the trimethylene-ring, it was important to prepare some of the other possible carboxylic acids, more especially the tricarboxylic acid (1, 2, 3), in which the three carboxyl-groups are attached to three different carbon-atoms, an acid which would therefore correspond with the hydromellitic acid of the benzene series—

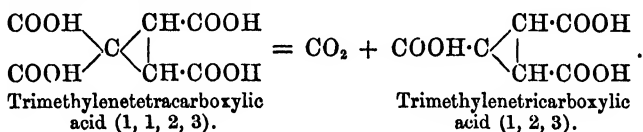


The synthesis of this acid may be accomplished in the following way:

When the sodium compound of malonic ether is heated with dibromosuccinic ether, a violent reaction sets in, sodic bromide is precipitated, and the ethyl salt of trimethylenetetracarboxylic acid (1, 1, 2, 3) is formed according to the equation—



On hydrolysis, the free tetracarboxylic acid is obtained, which on prolonged heating at 200° gives off carbonic anhydride, forming trimethylenetricarboxylic acid (1, 2, 3) thus—

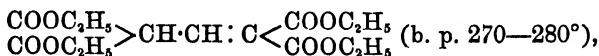


This synthesis is best carried out as follows: 4·5 grams of sodium are dissolved in 50 grams of absolute alcohol, and when cold mixed with 30 grams of ethyl malonate, 35 grams of ethyl dibromosuccinate (prepared by treating ethyl fumarate with bromine) are now slowly added. A violent reaction sets in after each addition of the bromosuccinate, so that it is necessary to add it in small quantities at a time and cool well during the operation. As soon as it is all added, the product, which has a deep yellow colour, is heated in a flask connected with a reflux condenser for about an hour on a water-bath, in order to ensure the reaction being complete. Water is then added, and the oil which is precipitated is several times extracted with ether. The ethereal solution is well washed with water, dried over calcic chloride, and the ether distilled off, when a quantity of an almost colourless oil remains behind, which is next roughly fractioned under diminished pressure (at 85 mm.). A large quantity distills below 150° (consisting principally of unchanged ethyl malonate), the thermometer then rises rapidly to 235°, between which temperature and 255° about half the weight of the original oil comes over. This is then several times very carefully fractioned under the same pressure, and at last obtained pure as a thick, colourless oil boiling constantly at 245—247° (85 mm.). The analysis gave the following numbers:—

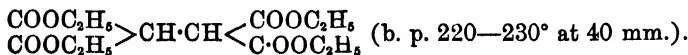
0·2377 gram substance gave 0·1532 gram H₂O and 0·4710 gram CO₂.

	Found.	Theory.
C	54·04 per cent.	$\begin{array}{c} \text{COOC}_2\text{H}_5 \diagup \text{C} \begin{array}{l} \text{CH} \cdot \text{COOC}_2\text{H}_5 \\ \text{CH} \cdot \text{COOC}_2\text{H}_5 \end{array} \diagdown \text{COOC}_2\text{H}_5 \end{array}$ 54·54 per cent.
H	7·16 ,,	6·67 ,,
O	38·80 ,,	38·79 ,,

The substance is therefore ethyl trimethylenetetracarboxylate (1, 1, 2, 3). It has an agreeable odour, and does not solidify at -10° . It is isomeric with ethyl dicarboxylglutaconate—*



and with ethyl propargylenetetracarboxylate—†



Trimethylenetetracarboxylic Acid (1, 1, 2, 3).

In order to obtain this acid, the pure ethyl-derivative was boiled for about five hours in a flask connected with a condenser, with a fairly concentrated solution of sodic hydrate, by which the oil was entirely saponified. The solution, which was slightly brownish, was then evaporated almost to dryness, acidified with dilute sulphuric acid (1 to 1), and extracted with pure ether. This extraction had to be repeated at least twenty times, as the acid is exceedingly soluble in water, in fact much more so than in ether. For this reason also any excess of water should be avoided. The ethereal solution was then carefully dried over calcic chloride, filtered, and the ether distilled off, great care being taken that the residue was not heated above 50° . By this means a very thick almost colourless oil was obtained, which after standing for some days over sulphuric acid in a vacuum, solidified almost entirely, forming curious circular masses very much resembling the mineral wavellite. In order to remove traces of oily matter, the crystals were first spread out on a porous plate, then repeatedly washed with benzene and light petroleum, and finally dried over sulphuric acid in a vacuum.

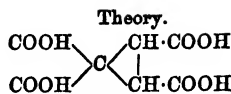
The following numbers were obtained on analysis :—

0·2643 gram substance gave 0·0816 gram H_2O and 0·3805 gram CO_2 .

* Conrad and Guthzeit (*Ber.*, 15, 2842).

† Schacherl (*Annalen*, 229, 91).

	Found.	Theory.
C	39·26 per cent.	38·53 per cent.
H	3·43 ,,	2·75 ,,
O	57·31 ,,	58·72 ,,



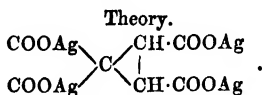
The acid was therefore trimethylenetetracarboxylic acid (1, 1, 2, 3). This acid, obtained in the way described above, is a hard colourless crystalline mass, which melts at 95—100°, being at the same time decomposed into trimethylenetricarboxylic acid and carbonic anhydride. It is easily soluble in water, ether, alcohol, and acetone, sparingly so in light petroleum, benzene, and toluene. The aqueous solution has a strongly acid reaction.

The *ammonium salt* is easily prepared by neutralising the aqueous solution of the acid with ammonia; it is extremely soluble in water. On adding argentic nitrate, the silver salt is obtained as a heavy white precipitate, which after collecting and washing with water, was dried over sulphuric acid in a vacuum and analysed with the following result :—

0·2773 gram substance gave 0·0196 gram H₂O and 0·1354 gram CO₂.

0·2038 gram substance gave 0·1350 gram Ag.

	Found.	Theory.
C	13·31 per cent.	13·00 per cent.
H	0·78 ,,	0·30 ,,
Ag	66·24 ,,	66·87 ,,
O	19·67 ,,	19·82 ,,



This salt is difficult to analyse. On warming, it decomposes suddenly, giving off a quantity of carbonic anhydride, and leaving a mass of silver threads. It is necessary, therefore, in order to get good numbers, to mix the salt thoroughly with finely divided oxide of copper, and conduct the combustion very slowly. The silver salt is, however, otherwise stable, and only slowly affected by exposure to light.

Barium chloride gives with the solution of the ammonium salt a white gelatinous precipitate of the *barium salt*, almost insoluble in water. The same salt is produced on adding an excess of baryta-water to an aqueous solution of the free acid.

The *copper salt* appears to be easily soluble in water. The *calcium salt* of this acid is the most characteristic. If a solution of

calcic chloride is added to the ammonium salt, no precipitate is produced; on warming, however, the calcium salt crystallises out in microscopic needles, which are much more soluble in cold than in hot water. The analyses show that this salt has the formula $C_7H_2O_8Ca_2 + H_2O$.

- I. 0.2670 gram substance lost, when heated at 130° for four hours, 0.0158 gram and gave 0.2276 gram $CaSO_4$.
 II. 0.2474 gram substance lost, when heated at 120° for five hours, 0.0146 gram and gave 0.2113 gram $CaSO_4$.

	Found.		
	I.	II.	
Ca.	25.07	25.12 per cent.	Theory. $C_7H_2O_8Ca_2 + H_2O$. 25.64 per cent.
H ₂ O	5.91	5.91 ,,	5.71 ,,

Trimethylenetricarboxylic Acid (1, 2, 3).

As has already been mentioned, trimethylenetetracarboxylic acid, when heated to 100° , melts and is decomposed, giving off carbonic anhydride, so that it is doubtful whether this is really the melting point or simply the decomposing point of the acid.

In order to obtain the tricarboxylic acid, it was found best to heat the tetracarboxylic acid to a temperature not exceeding 200° , otherwise a dark-coloured mass was obtained, which was difficult to purify. As soon as the evolution of carbonic anhydride had ceased, the whole was allowed to cool; a pale brown thick oily mass was obtained, which could not be made to crystallise. It was therefore dissolved in sodic hydrate, boiled for some time with freshly ignited animal charcoal, and filtered. The filtrate, which was almost colourless, was then acidified with dilute sulphuric acid, repeatedly extracted with ether, and the ethereal solution dried with calcic chloride. On distilling off the ether, an almost colourless oil remained behind, which, after standing for some days over sulphuric acid in a vacuum, almost entirely solidified. In order to purify these crystals as much as possible, they were first spread out on a porous plate, and lastly well washed with benzene and light petroleum. On account of the small quantity at my disposal, I was not able to obtain this acid in a more definitely crystalline condition.

The analyses gave the following results:—

- I. 0.1694 gram substance gave 0.0621 gram H_2O and 0.2583 gram CO_2 .
 II. 0.1459 gram substance gave 0.0525 gram H_2O and 0.2220 gram CO_2 .

	Found.			Theory.
	I.	II.		
C	41.59	41.49	per cent.	41.38 per cent.
H	4.07	3.99	"	3.45 "
O	54.34	54.52	"	55.17 "

Trimethylenetricarboxylic acid (1, 2, 3) had, therefore, been formed from the tetracarboxylic acid, by the simple splitting off of CO_2 , as shown on p. 823.

This acid melts at $150\text{--}153^\circ$; it is easily soluble in water, alcohol, and acetone, sparingly so in light petroleum, benzene, carbon bisulphide, and chloroform, and can be obtained in definite crystals by mixing the alcoholic solution with benzene, and allowing the whole to evaporate slowly at ordinary temperatures.

The free acid, when heated, first gives off water and then chars, a small quantity of a colourless oil distilling over, which solidifies on cooling. This sublimate is sparingly soluble in ether, and appears to be an anhydride of the acid.

The *ammonium* salt was next prepared by neutralising the aqueous solution with ammonia. On adding silver nitrate, a white amorphous precipitate was obtained, which, after well washing and drying, first over sulphuric acid and then at 130° , gave the following numbers on analysis:—

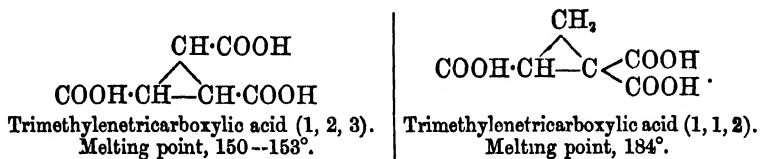
- I. 0.2890 gram substance gave 0.0266 gram H_2O , 0.1582 gram CO_2 , and 0.1880 gram Ag.
 II. 0.2418 gram substance gave 0.1575 gram Ag.

	Found.		Theory.
	I.	II.	
C	14.93	—	14.54
H	1.02	—	0.61
Ag	65.06	65.14	65.46
O	18.99	—	19.39

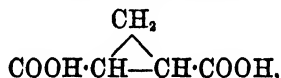
Cupric sulphate gives, with the ammonium salt, a beautiful light green precipitate, which is sparingly soluble in water. The barium and lead salts are white precipitates, almost insoluble in water. On adding calcic chloride to a dilute solution of the ammonium salt, no precipitate is formed. On warming, however, the calcium salt is precipitated in fine crystals; it is, as in the case of the calcium salt of the tetracarboxylic acid, more soluble in cold water than in hot.

It is remarkable that hydromellitic acid, which is the acid corre-

sponding with this acid in the benzene series, should also give a calcium salt, which is more easily soluble in cold than in hot water. Trimethylenetricarboxylic acid (1, 2, 3) is isomeric with the trimethylenetricarboxylic acid (1, 1, 2), obtained by Conrad and Guthzeit (*Ber.*, 17, 1185) by the action of α - β -dibromopropionic acid on ethyl malonate, as is easily seen from the following formulæ:—



The chief difference in these two acids is seen on their behaviour when heated. As already noticed, the acid (1, 2, 3) chars, giving only a trace of anhydride. The acid (1, 1, 2), on the contrary, containing two carboxyl-groups attached to one carbon-atom, is easily decomposed into the trimethylenedicarboxylic acid (1, 2),



and carbonic anhydride.

The trimethylenetricarboxylic acids are also isomeric with aconitic acid, carboxylglutaconic acid, &c. The acid (1, 2, 3) is, perhaps, identical with aconitic acid obtained by Baeyer (*Annalen*, 135, 206), by the action of sodium on ethyl monobromacetate.

ACTION OF ETHYLENE BROMIDE ON ETHYL ACETOACETATE.

In the preceding sections, I have described some derivatives of trimethylene which are produced by the action of ethylene bromide and ethyl dibromosuccinate on ethyl malonate. As, however, ethyl acetoacetate and ethyl benzoylacetate generally enter into the reactions in which ethyl malonate takes part, it seemed probable that by the study of the action of ethylene bromide on these compounds interesting trimethylene-derivatives might also be produced.

It was also thought that such derivatives prepared from ethyl benzoylacetate would probably be crystalline, and therefore easy to characterise.

In the following I shall, however, first describe the substances obtained by the action of ethylene bromide on ethyl acetoacetate, leaving the benzoyl-derivatives to a later chapter.



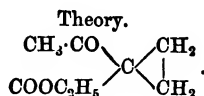
This ether, which is the principal product of the action of ethylene bromide on ethyl sodacetoacetate, is best prepared as follows:—To a solution of 5 grams of sodium in 60 grams of absolute alcohol, 26 grams of ethyl acetoacetate are slowly added, and then the whole heated with 20 grams of ethylene bromide in a soda-water bottle at 100° for eight hours. In carrying out this operation five such quantities, that is, 130 grams of ethyl acetoacetate, were generally worked with at once. At the end of this time a quantity of sodic bromide is precipitated, and the reaction is generally finished, as is proved by the product having a neutral reaction when diluted with water. After adding water, the oily layer which sinks to the bottom is separated from the aqueous liquid by means of a separating funnel, and dried over calcic chloride. The aqueous solution is then extracted once or twice with ether, well washed with water, dried over calcic chloride, and the ether distilled off. The oil which remains behind is then mixed with the principal product and the whole carefully fractioned with a column. Between 120–150°, a small quantity of unchanged ethylene bromide comes over, then the temperature rises rapidly to 180°, between which and 220° by far the greater part distils over, weighing about 120 grams. A considerable residue, however, always remains behind, with the examination of which I am at the present time engaged.

The fraction 180–220° still contained about 40 per cent. of unchanged ethyl acetoacetate; it was therefore further heated with 10 grams of sodium (dissolved in 120 grams of absolute alcohol) and 40 grams of ethyl bromide for 10 hours at 100°. The oil, after separating in the manner described above, was then refractioned, when the principal quantity again distilled over between 180° and 220°. This was now most carefully refractioned with a column until an oil was obtained which distilled over almost constantly between 195° and 200°. As analysis showed that this product still contained traces of ethyl acetoacetate, the whole was well shaken with a fairly concentrated aqueous potash solution for some hours, and then allowed to stand over night. By this means the ethyl acetoacetate dissolves, and is saponified, whereas most of the ethyl acetyltrimethylenecarboxylate remains unchanged. After extracting with ether and repeated fractioning, the product was probably almost pure, and boiled constantly between 197° and 200°. The analyses gave the following numbers:—

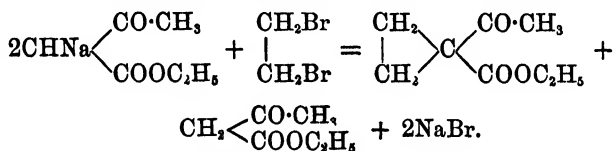
I. 0.1488 gram substance gave 0.1070 gram H₂O and 0.3337 gram CO₂.

- II. 0.2113 gram substance gave 0.1532 gram H_2O and 0.4735 gram CO_2 .
 III. 0.2512 gram substance gave 0.1833 gram H_2O and 0.5620 gram CO_2 .
 IV. 0.1773 gram substance gave 0.1276 gram H_2O and 0.3973 gram CO_2 .

	Found.					Theory.
	I.	II.	III.	IV.		
C	61.16	61.12	61.02	61.12	p. c.	61.54 p. c.
H	7.99	8.05	8.10	7.99	„	7.69 „
O	30.85	30.83	30.88	30.89	„	30.76 „



This compound is therefore ethyl acetyltrimethylenecarboxylate (1, 1) and is produced by the action of ethylene bromide on the sodium compound of ethylacetoacetate, according to the following equation:—



A vapour-density determination which was made by Hofmann's method, by vaporising the substance in a vacuum at 184° (aniline vapour), gave the following result:—

	Found.	Theory. $C_8H_{12}O_3$.
D.	4.94	5.39

Ethyl acetyltrimethylenecarboxylate is a peculiarly smelling colourless oil, boiling between 197° and 200° . It does not solidify at 0° . The sp. gr. and magnetic rotation determinations, which were performed by my father, gave the following numbers:—

Density:—

$$\begin{array}{ll} d_{4^\circ}^{4^\circ} = 1.03436. & d_{6.5^\circ}^{6.5^\circ} = 1.03256. \\ d_{15^\circ}^{15^\circ} = 1.02549. & d_{25^\circ}^{25^\circ} = 1.01834. \end{array}$$

Magnetic rotations :—

<i>t.</i>	Sp. rotation.	Mol. rotation.
12·5	1·1696	9·865
12·5	1·1596	9·780
12·5	1·1643	9·820
12·5	1·1623	9·802
Average... 12·5	1·1639	9·817

Dr. Gladstone was so kind as to determine the refractive equivalent, and gave me the following account of his results.

Temp.	μ_A .	μ_D	μ_H .	Specific refraction A.	Specific dispersion.	Refractive equivalent A.
22°	1·4600	1·4667	1·4910	0·4517	0·0305	70·46

"If the ethyl acetyltrimethylenecarboxylate were a member of the series below the tetramethylene compound* I examined before, it ought to give a refractive equivalent of 68: the equivalent found, 70·46, indicates an additional pair of double linked carbon-atoms; this seems perplexing, especially as the dispersion does not indicate any increase in that direction."

The yield of ether obtained by the above method is not good, a quantity of high-boiling oil being produced at the same time; this appears to be the product of the action of 1 mol. of ethylene bromide on 2 mols. of ethyl acetoacetate.

When treated with phosphorous pentachloride, ethyl acetyltrimethylenecarboxylate is violently attacked, chlorinated bodies being formed which are at present under examination.

On warming with alcoholic potash, the ether is easily saponified. It appears to combine with hydroxylamine and phenylhydrazine, forming thick oils, which as they could not be obtained crystalline were not further examined.

Acetyltrimethylenecarboxylic Acid (1, 1).

In order to obtain this acid, the pure ether was mixed with an excess of a fairly concentrated solution of alcoholic potash, and then allowed to stand at ordinary temperatures to saponify. In a short

* I hope to be able to have the honour of laying an account of this substance before the Society in a short time.

time, crystals of a potassic salt separated, the liquid becoming slightly brownish. At the end of about five days water was added, and any unchanged ether carefully separated from the potassic salt by repeated treatment with ether. The aqueous solution was then acidified with dilute sulphuric acid, and several times extracted with small quantities of ether. The ethereal solution after being well washed and dried over calcic chloride was evaporated on a water-bath, when the crude acid was left as a thick slightly brownish oil, which did not solidify after standing for some days over sulphuric acid in a vacuum.

In order to purify this crude product, it was dissolved in dilute sodic carbonate, and after warming on a water-bath, well shaken with animal charcoal and filtered; by this means an almost colourless solution of the sodic salt was produced, which was then acidified with sulphuric acid, and extracted repeatedly with pure ether. The ethereal solution, after carefully drying over calcic chloride and evaporating, deposited an almost colourless oil; this after standing for some days over sulphuric acid in a vacuum gave the following numbers on analysis:—

0.1624 gram substance gave 0.0975 gram H_2O and 0.3375 gram CO_2 .

	Found.	Theory.
C	56.68 per cent.	$\begin{array}{c} CH_3.CO \\ COOH \end{array} \diagup \begin{array}{c} CH_2 \\ \\ CH_2 \end{array}$ 56.25 per cent.
H	6.67 "	6.25 "
O	36.65 "	37.50 "

The substance was therefore acetyltrimethylenecarboxylic acid (1, 1). This acid is fairly easily soluble in water, the solution being strongly acid to test-paper. It does not solidify when kept at -10° for some hours, but becomes so thick that the vessel containing it may be turned over without any of the substance falling out. The solution in alkalis is easily decomposed on adding iodine, iodoform being formed in abundance. Sodic hypochlorite also produces chloroform when added to a solution of the acid in sodic carbonate. On warming in a test-tube above 100° , the acid is decomposed, carbonic anhydride being driven off, and neutral oils formed, which will be more fully described later on.

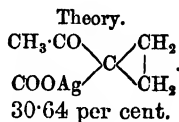
The salts of acetyltrimethylenecarboxylic acid are very characteristic.

The ammonium salt is easily prepared by dissolving the acid in a slight excess of ammonia and allowing the solution to evaporate over sulphuric acid in a vacuum. It crystallises in colourless needles, which are very soluble in water.

The *silver salt* is obtained by adding nitrate of silver to the hot solution of the ammonium salt. On cooling, it crystallises out in nodular masses, which consist of a mass of fine needles. These were first dried between filter-paper and then over sulphuric acid in a vacuum. The analysis gave the following numbers:—

- I. 0.2693 gram substance gave 0.0791 gram H_2O , 0.3053 gram CO_2 , and 0.1223 gram Ag.
 II. 0.4212 gram substance gave 0.1938 gram Ag.
 III. 0.3224 " " 0.1470 "

	Found.			Theory.
	I.	II.	III.	
C	30.92	—	—	30.64 per cent.
H	3.26	—	—	2.98 "
Ag	45.41	46.01	45.60	45.95 "
O	20.41	—	—	20.42 "



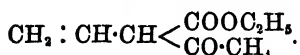
This salt is very stable, and only slowly darkened when exposed to the influence of diffused light.

If a solution of *ferric chloride* is added to the ammonium salt, a dark brown precipitate is formed, which on boiling dissolves, producing a dark red solution. *Ferrous sulphate* gives no precipitate. *Mercuric chloride*, with a solution of the ammonium salt, gives a white curdy precipitate, which on boiling dissolves, and crystallises out again in needles on cooling. *Mercurous chloride* gives a black precipitate. Baric chloride, calcic chloride, magnesian sulphate, stannous chloride, and nickelous sulphate, do not give any precipitate with the ammonium salt. The *lead salt* is a white precipitate soluble in hot water.

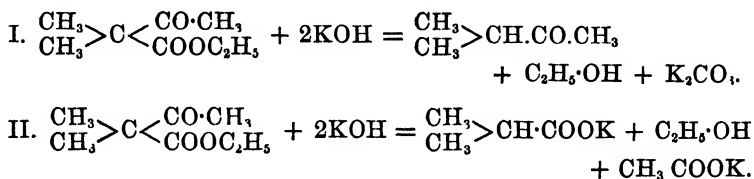
Acetyltrimethylenecarboxylic acid in alkaline solutions is a very stable compound; it may be boiled with alcoholic potash for a considerable time without being decomposed.

When boiled with dilute sulphuric acid, it is easily split up, abundance of carbonic anhydride being given off, and a dark brownish oil remaining behind; on extracting this with ether and fractioning, it could not be obtained pure, and appeared to be a mixture of several bodies. The same decomposition occurs on boiling the acid with water alone, the residual oil, however, appears to be purer.

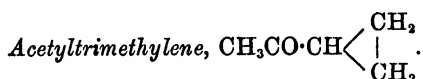
From the stability not only of the acid itself, but more especially of its salts, as will have been noticed from the above description, it is clear that this acid, or rather its ethereal salt, is something quite different from ordinary substituted ethyl acetoacetates. From the method of its formation, it must, however, be either ethyl acetyltrimethylenecarboxylate or an ethyl vinylacetoacetate of the formula



All acetoacetic ethers, as is well known, are easily split up on boiling with potash into acids and ketones. Thus ethylic dimethylacetoacetate (which only differs from ethylic acetyltrimethylenecarboxylate by two hydrogen-atoms) gives on hydrolysis isopropyl methyl ketone, dimethylacetic acid, acetic acid, and carbonic anhydride, thus:—



It was only by using great precautions that Ceresole (*Ber.*, 15, 1874) succeeded in obtaining dimethylacetoacetic acid, and found that this acid was extremely unstable, being slowly and completely decomposed, even at ordinary temperatures, into isopropyl methyl ketone and carbonic anhydride—a behaviour very different to that of acetyltrimethylenecarboxylic acid, which can be kept for weeks without the slightest decomposition setting in. The salts of dimethylacetoacetic acid are, moreover, almost as unstable as the acid itself: thus the silver salt is decomposed directly on warming, silver being precipitated, whereas the silver salt of acetyltrimethylenecarboxylic acid can be recrystallised from boiling water without decomposition. It is evident that a very great difference exists between the latter acid and all the substituted acetoacetic acids which have been prepared, and which behave in a way perfectly analogous to dimethylacetoacetic acid. There can, therefore, be no doubt that the acid is not a vinylacetoacetic acid, but that it is really acetyltrimethylenecarboxylic acid (1, 1).



As has already been mentioned, acetyltrimethylenecarboxylic acid is easily decomposed on boiling with water or dilute acids into neutral oils and carbonic anhydride, and, as it was thought that it would be interesting to follow up this reaction, several such decomposition experiments were tried, and the oils produced carefully examined without any definite result. It was then found that the acid itself underwent a similar decomposition when distilled, carbonic anhydride and low-boiling oils being given off, and, as it appeared likely that the latter might be more easy to purify than those produced by boiling

with dilute acids, the careful examination of the product was undertaken with the following results:—

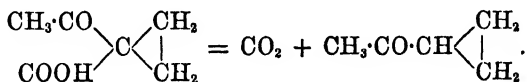
A considerable quantity of acetyltrimethylenecarboxylic acid was, in portions of 5 grams at a time, heated at 200° in a retort connected with a condenser until the evolution of carbonic anhydride ceased. During the operation, a colourless oil distilled over leaving a considerable residue in the retort, which I have not as yet been able to examine.

The distillate was next carefully fractioned in a Würtz flask with a long neck, and the fraction 100—125° collected separately. This was then repeatedly refractioned until at last a beautiful colourless oil was obtained boiling constantly at 112—113° (at 720 mm.). It gave the following numbers on analysis:—

0.1915 gram substance gave 0.1663 gram H₂O and 0.4994 gram CO₂.

	Found.	Theory. $\text{CH}_3\cdot\text{CO}\cdot\text{CH}\begin{matrix} \diagup \text{CH}_2 \\ \\ \text{CH}_2 \end{matrix}$.
C	71.12 per cent.	71.42 per cent.
H	9.64 „	9.52 „
O	19.24 „	19.05 „

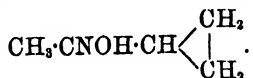
This substance was therefore acetyltrimethylene or trimethylene methyl ketone. It is produced from acetyltrimethylenecarboxylic acid by the splitting off of carbonic anhydride according to the equation—



Acetyltrimethylene is a colourless, mobile oil, of powerful odour, recalling somewhat that of camphor. It appears to be easily polymerised, particularly when treated with acids, high-boiling oils, which at present have not been further examined, being formed.

The yield of acetyltrimethylene from acetyltrimethylenedicarboxylic acid is comparatively small, owing to the production of these more complicated condensation-products.

Acetyltrimethylene unites with hydroxylamine, producing a compound which crystallises in needles; it is probably the oxime—



Unfortunately the quantity at my disposal was too small to admit of analysis.

ACTION OF ETHYLENE BROMIDE ON ETHYL BENZOYLACETATE.



In previous researches on ethyl benzoylacetate (Trans., 1884, 170) I have shown that it is not only capable of entering into all the reactions in which ethyl acetoacetate takes part, but that, on account of the power of crystallising possessed by its derivatives, it is a much more convenient substance for use in synthetical researches than the acetoacetate. On studying the action of ethylene bromide on ethyl benzoylacetate, it was found, as was to be expected, that compounds exactly analogous to those produced by the action of ethylene bromide on ethyl acetoacetate were formed, the acetyl-group in the latter derivatives being replaced by the benzoyl-group. In carrying out this reaction the following method was found to give the best results.

5 grams of sodium are dissolved in 60 grams of absolute alcohol, and then a mixture of 40 grams of ethyl benzoylacetate and 20 grams of ethylene bromide slowly added, care being taken that the mixture does not get hot. The whole is then heated in a soda-water bottle to 100° for six hours, at the end of which time the reaction is complete. The dark brownish-coloured mass is now mixed with about three times its volume of water and several times extracted with ether, the ethereal solution being well washed with water and carefully dried over calcic chloride. On distilling off the ether, a dark-brown oil remains behind, consisting of ethyl benzoyltrimethylenecarboxylate and unchanged ethyl benzoylacetate. This oil is further digested with 1·5 grams of sodium (dissolved in absolute alcohol) and 8 grams of ethylene bromide at 100° for six hours, and then treated as described above. A dark-brown oil is thus obtained which, besides ethyl benzoyltrimethylenecarboxylate, still contains some unchanged ethyl benzoylacetate which is very difficult to completely remove by fractional distillation. It is best, therefore, to convert it into the free acid in the following way:—The crude product is mixed with an excess of a fairly concentrated solution of alcoholic potash and allowed to stand at ordinary temperatures for about seven days, in order that the ether may be completely saponified. On adding water, a considerable quantity of oil is precipitated (consisting principally of ethylene bromide, acetophenone, and a little unchanged ether) and must be removed by repeated treatment with ether.

The alkaline solution is then acidified with dilute sulphuric acid, when a thick brownish-coloured oil is precipitated, which is several times extracted with ether. The ethereal solution, after well washing

and drying over calcic chloride, deposits the crude acid on evaporation, as a thick reddish-brown oil, which, on standing over sulphuric acid in a vacuum, deposits a quantity of crystals.

The whole mass is, however, best purified by redissolving it in hot sodic carbonate, agitating well with animal charcoal for about half an hour, and filtering.

A much lighter coloured solution of sodic salt is thus obtained, which is again acidified with dilute sulphuric acid and extracted with ether.

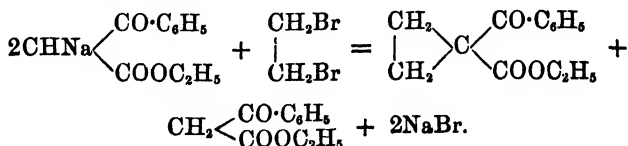
On evaporation, the ethereal solution deposits an oil, which, although still dark-coloured, usually solidifies almost completely on standing over sulphuric acid in a vacuum for a few days. The crystals are next roughly purified from the oily mother-liquor by spreading out on a porous plate, when they become almost colourless. The mass of crystals is dissolved in ether, and the solution concentrated on a water-bath till crystallisation sets in. If this solution be now allowed to concentrate further by evaporation at ordinary temperatures, the benzoyltrimethylenecarboxylic acid crystallises out in magnificent colourless prisms, which are pure when once recrystallised.

Besides this acid, the mother-liquors contain benzoic acid, which, however, on account of its greater solubility in ether, is easy to get rid of by repeated crystallisation from this solvent. The analysis of the pure acid gave the following results:—

- I. 0.1867 gram substance gave 0.0888 gram H_2O and 0.4737 gram CO_2 .
 II. 0.2143 gram substance gave 0.1048 gram H_2O and 0.5482 gram CO_2 .

	Found.		Theory.
	I.	II.	
C	69.19	69.77	69.47 per cent.
H	5.28	5.43	5.27 ,,
O	25.53	24.80	25.26 ,,

This substance was, therefore, benzoyltrimethylenecarboxylic acid (1, 1), its ethereal salt being formed by the action of ethylene bromide on ethyl benzoylacetate thus:—



Benzoyltrimethylenecarboxylic acid melts at 148—149°, being decom-

posed at the same time into carbonic anhydride and benzoyltrimethylene, a compound which will be fully described later on.

It is fairly easily soluble in ether, chloroform, benzene, and bisulphide of carbon; sparingly in water. If, however, the acid is dissolved in ammonia, it is precipitated in a very finely divided state on adding dilute sulphuric acid. Thus prepared it dissolves, although with difficulty, in boiling water, and crystallises out on cooling in long colourless needles, which appear to have a slightly higher melting point than the acid crystallised from other solvents. The acid crystallises best, however, from ether. If the concentrated ethereal solution be allowed to evaporate slowly, most magnificent colourless prisms are obtained, which Professor Haushofer was kind enough to examine. He gave me the following description of this body:—

Crystalline System, Monoclinic.

$$a : b : c = 2.3298 : 1 : 2.1319.$$

$$\beta = 83^\circ 4'.$$



Pale yellow transparent crystals with the combinations $OP(c)$, $\infty P(p)$, $\infty P\infty(a)$, $-\infty P\infty(r)$, $\infty P\infty(s)$; tabular in the direction of the face c , usually elongated in the direction of the orthodiagonal. The face c is usually bent somewhat concave; cleavage imperfect in the direction p .

	Measured.	Calculated.
$a : c =$	$96^\circ 56'$	—
$a : r =$	$136 \quad 13$	—
$p : p =$	$133 \quad 14$	—
$s : a =$	$128 \quad 42$	$128^\circ 40'$
$r : c =$	$140 \quad 38$	$140 \quad 43$
$p : c =$	$92 \quad 50$	$92 \quad 45$

Although a certain general morphological resemblance between this compound and the carboxylic acid of benzoyltetramethylene can be observed, as for example in the relation of the angles $c : r$, in the

basal angles ($23^{\circ} 14'$ and $20^{\circ} 46'$), or in the relation of the axes $a:b$, no inference can be safely drawn from these circumstances.

The *ammonium* salt of this acid is easily prepared by dissolving the pure acid in an excess of ammonia and allowing the solution to evaporate over sulphuric acid in a vacuum. It is thus obtained as a colourless, crystalline mass, very easily soluble in water. On adding dilute acids to a solution of the ammonium salt, the acid is precipitated in a pure condition as a mass of minute colourless needles. If nitrate of silver is added to the solution of the ammonium salt, the silver salt is obtained as a white curdy precipitate insoluble in water. After well washing and drying over sulphuric acid in a vacuum, the following numbers were obtained on analysis:—

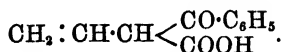
0.2352 gram substance gave 0.0677 gram H_2O , 0.3817 gram CO_2 , and 0.0854 gram Ag.

	Found.	Theory.
C.	44.26 per cent.	$ \begin{array}{c} C_6H_5 \cdot CO \\ \diagdown \quad \diagup \\ C \\ \diagup \quad \diagdown \\ COOAg \quad CH_2 \\ \quad \quad \\ \quad \quad CH_2 \end{array} $
H	3.20 „	44.44 per cent.
Ag	36.31 „	3.04 „
O	16.23 „	36.36 „
		16.16 „

This salt is very stable, and is only slowly darkened when exposed to diffused light.

Ferric chloride gives with a solution of the ammonium salt a reddish-white precipitate, which, on warming, becomes slightly darker coloured. *Ferrous sulphate*, *baric chloride*, and *calcic chloride* give no precipitates. The *copper salt* is obtained on adding cupric sulphate to the ammonium salt, as a light green precipitate, which is sparingly soluble in water. *Plumbic acetate* gives with the ammonium salt a heavy white precipitate, which dissolves, although with difficulty, in boiling water, and on cooling crystallises out in small colourless needles. All these salts are very stable.

Benzoyltrimethylenecarboxylic acid itself may be boiled for a long time with strong solutions of alcoholic potash without any appreciable change taking place. On preparing this acid, however, from the crude ethereal salt, it is better to saponify at ordinary temperatures, and not to boil, as the impurities present, such as ethyl benzoylacetate, acetophenone, &c., are liable to be changed into resinous bodies, which render the further purification of the acid a matter of great difficulty. The stability of this acid towards alkalis is quite as remarkable, if not more so, than that of acetyltrimethylenecarboxylic acid, and it is quite out of the question to suppose that it has the constitution of a substituted vinylbenzoylacetic acid of the formula—



As I have shown in previous researches, it is practically impossible to obtain the substituted benzoylacetic acids by the hydrolysis of their ethers at ordinary temperatures. On warming with potash, they are naturally completely split up, not a trace of the corresponding acids being left.



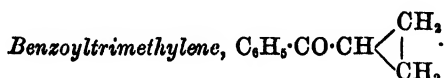
In order to obtain this in a pure state, the silver salt of benzoyltrimethylenecarboxylic acid was mixed with a slight excess of ethyl iodide and a little pure ether, and heated in a flask connected with a reflux condenser for about two hours on a water-bath. The silver salt was thus easily decomposed. After filtering from the precipitated iodide of silver, the ethereal solution was evaporated on a water-bath, when a colourless oil remained behind; this on distillation went over completely between 280° and 290° . On refractioning, by far the greater part distilled over between 280° and 283° (720 mm.), as an almost colourless oil, which gave the following numbers on analysis:—

- I. 0.1359 gram substance gave 0.0793 gram H_2O and 0.3540 gram CO_2 .
 II. 0.1312 gram substance gave 0.0765 gram H_2O and 0.3446 gram CO_2 .

	Found.		Theory.
	I.	II.	
C	71.04	71.63	71.56 per cent.
H	6.48	6.47	6.42 „
O	22.48	21.90	22.02 „

The substance was therefore ethyl benzoyltrimethylenecarboxylate (1, 1). It is a thick colourless oil, possessing a faintly aromatic odour and burning taste. It does not appear to solidify when exposed to a temperature of -10° .

It distils without the least decomposition at $280-283^\circ$ (720 mm.), and is easily saponified by warming with alcoholic potash, benzyltrimethylenecarboxylic acid being regenerated.



As already mentioned, benzoyltrimethylenecarboxylic acid, when

heated a few degrees above its melting point, is completely decomposed, carbonic anhydride being given off, and a yellowish oil remaining behind, which on cooling does not again solidify. As it was thought that interesting results might be obtained by following up this decomposition, 9 grams of the pure acid were heated in an oil-bath at 200° , until no more carbonic anhydride was evolved. The residue, which was a thick brownish-coloured oil, was then carefully fractioned, almost the whole (about 6.1 grams) distilling over between 235° and 242° . This distillate was then once or twice refractioned, and thus easily obtained perfectly pure as an almost colourless oil boiling constantly at $239-239.5^{\circ}$ (720 mm.).

The analyses gave the following results:—

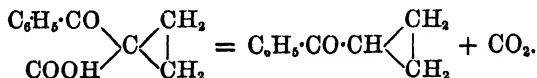
- I. 0.1730 gram substance gave 0.1114 gram H_2O and 0.5205 gram CO_2 .
 II. 0.1382 gram substance gave 0.0920 gram H_2O and 0.4150 gram CO_2 .
 III. 0.1597 gram substance gave 0.1014 gram H_2O and 0.4791 gram CO_2 .

	Found.				Theory.
	I.	II.	III.		$C_6H_5 \cdot CO \cdot CH \begin{matrix} \diagup CH_2 \\ \diagdown CH_2 \end{matrix}$
C	82.05	81.90	81.82	per cent.	82.19 per cent.
H	7.15	7.39	7.05	"	6.85 "
O	10.80	10.71	11.13	"	10.96 "

The vapour-density of this compound was determined by Hofmann's method by volatilising the substance in a vacuum in aniline vapour. The following numbers were obtained:—

	Found.		Theory.
	I.	II.	$C_6H_5 \cdot CO \cdot CH \begin{matrix} \diagup CH_2 \\ \diagdown CH_2 \end{matrix}$
D	5.34	5.21	5.04

This substance was, therefore, without doubt benzoyltrimethylene. It is formed from benzoyltrimethylenecarboxylic acid by the simple splitting off of carbonic anhydride, according to the equation—



Benzoyltrimethylene is a colourless oil, of aromatic odour, which does not solidify when cooled down to -10° . It is formed almost quantitatively according to the above equation. 9 grams of benzoyltrimethylenecarboxylic acid should give 6.9 grams of benzoyltri-

methylene, and in the experiment 6.1 grams were obtained boiling between 235° and 242° , which, allowing for loss by distillation, is as much as could be expected when such small quantities are operated with. It is rather curious that such a good yield should be obtained, when it is remembered that the amount of acetyltrimethylene obtained by the decomposition of acetyltrimethylenecarboxylic acid is so small. The acetyl-derivative appears, therefore, to be less stable than the benzoyl one.

Benzoyltrimethylene is not affected when treated with bromine at ordinary temperatures; on heating, however, substitution takes place, abundance of hydrobromic acid being evolved. The product, after washing with sodic carbonate solution, is a colourless, very heavy oil, which, however, owing to the small amount at my disposal, could not be further examined. The solution of benzoyltrimethylene in chloroform can be boiled for a considerable time with bromine without any appreciable change taking place, a proof that it cannot be unsaturated.

ACTION OF HYDROBROMIC ACID ON BENZOYLTRIMETHYLENecARBOXYLIC ACID (1, 1).

ω-Bromopropyl Phenyl Ketone, $C_6H_5 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH_2Br$.

It has already been shown (p. 814) that trimethylenedicarboxylic acid (1, 1), when treated with fuming hydrobromic acid, is converted into bromethylmalonic acid, the trimethylene-ring being split. This result confirms the remarkable observations of Freund (*loc. cit.*, p. 818), that the trimethylene-ring, although very stable when treated with bromine, is easily decomposed when acted on by fuming hydrobromic or hydriodic acid. It was thought advisable to further prove this point, if possible, by subjecting other differently constituted trimethylene-derivatives to the same treatment. It appeared probable that benzoyltrimethylenecarboxylic acid, being such a beautifully crystalline substance, might be expected to give well-defined decomposition products, which could easily be purified and identified; on this account it seemed to be especially adapted for further examination.

The pure acid was first obtained in a finely divided condition by dissolving it in ammonia and precipitating with dilute sulphuric acid; the sandy mass was then well washed and dried over sulphuric acid in a vacuum.

On mixing the dry substance with fuming hydrobromic acid (sp. gr. 1.83) it did not dissolve, and no reaction was at first perceptible. After standing, however, for about an hour, at ordinary temperatures,

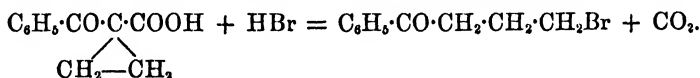
small bubbles began to appear, and on agitating a quantity of gas was evolved which proved to be carbonic anhydride. This evolution of carbonic anhydride lasted for about a week, at the end of which time the decomposition was complete, the liquid dividing into two distinct layers, the upper one, which was a brownish oil, being the product of the reaction. This was separated, dissolved in a little ether, and well shaken with a dilute solution of sodic carbonate in order to remove any excess of hydrobromic acid.

After drying over potassic carbonate and distilling off the ether, a slightly brownish-coloured oil remained behind, which, however, soon solidified to a hard crystalline mass. The substance, which is practically pure, can be freed from minute traces of mother-liquor by spreading it out on a porous plate. It then gave the following numbers on analysis:—

- I. 0.1924 gram substance gave 0.0849 gram H_2O and 0.3703 gram CO_2 .
 II. 0.3070 gram substance gave 0.2510 gram $AgBr$.

	Found.		Theory. $C_6H_5 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH_2Br$.
	I.	II.	
C	52.49	—	52.86
H	4.90	—	4.85
Br	—	35.93	35.24
O	—	—	7.05

It is, therefore, ω -bromopropyl phenyl ketone.* It is formed from benzoyltrimethylenecarboxylic acid (1, 1) according to the equation—



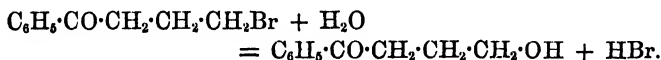
This reaction is perfectly analogous to the formation of γ -bromethylmalonic acid from trimethylenecarboxylic acid (1, 1).

ω -Bromopropyl phenyl ketone melts at $37-39^\circ$. It is easily soluble in light petroleum, methyl alcohol, ethyl alcohol, chloroform, ether, carbon bisulphide, benzene, acetone, and ethyl acetate, but is insoluble in water. It is precipitated from its solutions on evaporation always as an oil, and cannot, therefore, be purified by recrystallisation. The oily drops when touched with a glass rod directly solidify.

When boiled with a dilute solution of silver nitrate, this compound is easily decomposed, quantities of silver bromide being precipitated, and an oily body formed; owing to the small quantity at my disposal, it could not be further examined.

* With regard to the nomenclature of this body, see Baeyer (*Ber.*, 17, 960).

Bromethylmalonic acid behaves in exactly the same way, being converted into carbobutyrolactone; it is probable that this decomposition product of *ω*-bromopropyl phenyl ketone is *ω*-hydroxypropyl phenyl ketone, formed according to the following equation:—

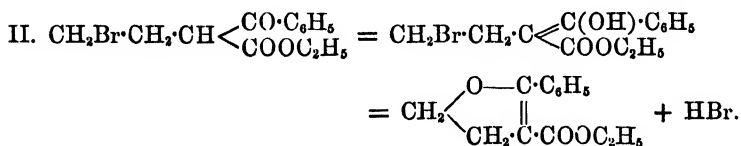
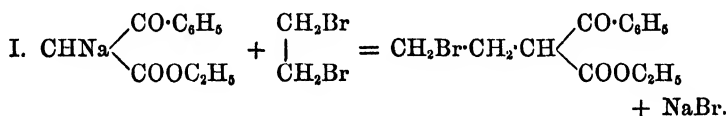


Alcoholic potash appears to have the same effect. *ω*-Bromopropyl phenyl ketone is formed with still greater ease when benzoyltrimethylene is allowed to stand for some time with fuming hydrobromic acid. From these experiments, it would appear that the remarkable splitting of the trimethylene-ring under the influence of the halogen acid takes place, with even greater ease in the case of the derivatives than of the hydrocarbon itself.

Action of Hydroxylamine on Benzoyltrimethylene.

In the action of ethylene bromide on ethyl malonate, there are only two interpretations of the reaction, namely, (1) that a trimethylene-derivative or (2) that a vinyl-derivative is formed.

As soon as ethyl malonate is replaced by ethyl benzoylacetate, however, a third possibility comes into account, namely, that the reaction could take place according to one of the following equations:—

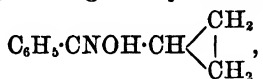


Such a reaction, although improbable, is still by no means impossible, and it appeared necessary in this case also to bring some decided experimental proof to bear on the question. According to the above series of equations, benzoyltrimethylene would have the

formula $\text{CH}_2 \begin{array}{l} \diagup \text{O}\cdot\text{C}_6\text{H}_5 \\ \diagdown \text{CH}_2\cdot\text{CH} \parallel \end{array}$, that is, be a furfurane-derivative and not a

ketone. In order to decide this, it was only necessary to treat benzoyltrimethylene with hydroxylamine and see whether it formed an oxime

or not. The experiment showed that it combined with hydroxylamine like all other ketones, forming benzoyltrimethyleneoxime,



a definite proof that it contained the ketone-group CO, and, therefore, could not be a furfurane-derivative. In preparing the oxime, the following method was found to give the best results:—3 grams of benzoyltrimethylene are dissolved in a little alcohol, and then a mixture of 4 grams of hydroxylamine hydrochloride and 3 grams of potassic carbonate dissolved in a small quantity of water are added, the quantities of alcohol and water being so regulated that the benzoyltrimethylene remains completely dissolved. The whole is allowed to stand for about a week at ordinary temperatures to ensure the completion of the reaction, then acidified with a little dilute sulphuric acid and extracted once or twice with ether. The ethereal solution, after well washing with water to remove the alcohol as much as possible, is dried over calcic chloride and evaporated, when a thick colourless oil remains behind; this almost completely solidifies on standing over sulphuric acid in a vacuum for a short time.

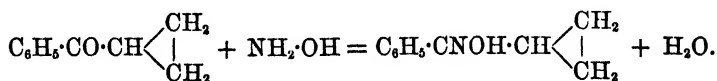
The crystals, after being spread out on a porous plate to roughly remove traces of mother-liquor and then recrystallised from ether, are easily obtained pure. The analysis gave the following results:—

I. 0.2107 gram substance gave 0.1330 gram H_2O and 0.5741 gram CO_2 .

II. 0.2748 gram substance gave 21.5 c.c. N. $t = 17^\circ$. Bar. = 718 mm.

	Found.		Theory. $\text{C}_6\text{H}_5\cdot\text{CNOH}\cdot\text{CH}\begin{array}{c} \text{CH}_2 \\ \\ \text{CH}_2 \end{array}$.
	I.	II.	
C	74.31	—	74.53 per cent.
H	7.01	—	6.84 „
N	—	8.61	8.69 „
O	—	—	9.93 „

Benzoyltrimethyleneoxime had therefore been formed according to the equation—



Benzoyltrimethyleneoxime melts at $86-87^\circ$. It crystallises from light petroleum, boiling at $50-70^\circ$, in curiously striped leafy masses which are colourless when pure. It can be obtained in beautiful

prisms by allowing the ethereal solution to evaporate slowly. It is easily soluble in ether, benzene, chloroform, alcohol, and carbon bisulphide, sparingly so in cold light petroleum. It appears to be completely decomposed on long keeping, the crystals disappearing and an uninviting brownish oil being formed.

A result totally different from the preceding is obtained when benzoyltrimethylene is heated with hydroxylamine and hydrochloric acid in a sealed tube, the reaction being much more complicated. If a mixture of 4 grams of benzoyltrimethylene, 4 grams of hydroxylamine hydrochloride, 30 grams of absolute alcohol, and a few drops of hydrochloric acid be digested in a sealed tube at 130—140°, the mixture becomes darker and darker coloured till at the end of six hours the tube appears to be perfectly black. If, however, a small quantity of the contents be taken out and diluted with alcohol the whole dissolves, producing a beautiful deep-blue solution which in reflected light shows an intense brick-red fluorescence. The colour being so beautiful it was thought that it would be interesting to further examine the same in order if possible to see what relation existed between it and benzoyltrimethyleneoxime. All attempts to obtain the product, which proved to be a mixture of the hydrochlorides of two bases, in a crystalline condition being unsuccessful, it was decomposed with alkali and the free bases themselves worked on. To obtain the bases, the contents of several such tubes as those described above were dissolved in alcohol, gently warmed on a water-bath, and then agitated with a dilute solution of sodic carbonate. The beautiful blue colour instantly disappeared and a brownish-red precipitate was formed which, after standing for a short time, was collected, thoroughly washed with water until free from inorganic matter, and then dried over sulphuric acid in a vacuum. The blackish-red amorphous mass thus obtained was next treated with various solvents in the hope of obtaining something crystalline for analysis, but without result. It was, however, soon discovered that the product was not homogeneous, but consisted of two distinct bases, one of which was fairly easily soluble, the other almost insoluble in ether. In order to separate these, the crude substance was first obtained in as finely-divided condition as possible by powdering under water and then repeatedly extracted with pure ether, until a residue was left which did not further dissolve, and which will be described in detail further on.

The dark brownish-red ethereal extract was next washed with water, carefully dried over potassic carbonate, and the ether distilled off. By this means a blackish, semi-solid mass remained behind which, on standing over sulphuric acid, soon became hard and brittle, but could not by any means be obtained in a crystalline condition.

It was powdered, carefully dried over sulphuric acid in a vacuum, and analysed with the following results:—

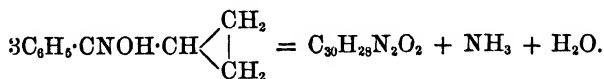
- I. 0.1780 gram substance gave 0.1009 gram H_2O and 0.5244 gram CO_2 .
 II. 0.1737 gram substance gave 0.0984 gram H_2O and 0.5113 gram CO_2 .
 III. 0.1824 gram substance gave 0.1049 gram H_2O and 0.5384 gram CO_2 .
 IV. 0.2188 gram substance gave 12.4 c.c. N. $t = 21^\circ$. Bar. = 718 mm.
 V. 0.3055 gram substance gave 18.1 c.c. N. $t = 24^\circ$. Bar. = 718 mm.
 VI. 0.2699 gram substance gave 16.1 c.c. N. $t = 22^\circ$. Bar. = 718 mm.

	Found.					
	I.	II.	III.	IV.	V.	VI.
C	80.35	80.28	80.45	—	—	— p. c.
H	6.29	6.29	6.39	—	—	—
N	—	—	—	6.09	6.23	6.28 „

Theory. $\text{C}_{30}\text{H}_{28}\text{N}_2\text{O}_2$.	
C	80.36 per cent.
H	6.25 „
N	6.25 „
O	7.14 „

Analyses I, II, IV, and V were done with the sample first prepared, III and VI from a later preparation; it would, therefore, seem as though the body were homogeneous.

This base has, therefore, the formula $\text{C}_{30}\text{H}_{28}\text{N}_2\text{O}_2$, and is possibly formed from 3 mols. of benzoyltrimethyleneoxime according to the equation:



It is easily soluble in acetone, aniline, and nitrobenzene, forming brownish-red solutions; it is more sparingly soluble in ether, alcohol, benzene, and toluene. On allowing the solution in acetone to evaporate at ordinary temperatures, the base is precipitated as a blackish-red, semi-solid mass which, on standing, soon becomes hard and brittle. When broken up, it has a shining surface somewhat resembling that of ordinary pitch.

It dissolves in acetic acid forming a greyish-blue solution which

contains the acetate of the base. If the brownish-red alcoholic solution is treated with zinc-dust and ammonia it is reduced and becomes colourless; on shaking with air it is reoxidised, the colour again appearing. Distilled with zinc-dust, the base is entirely broken up, oily bodies being given off which have a peculiar odour recalling somewhat that of aniline. When distilled with soda-lime, a heavy oil comes over in considerable quantity which possesses in a marked way the characteristic smell of benzonitrile.

The salts of this base are easily obtained by adding dilute acids to its alcoholic solution. They are deep blue, and the solutions possess a most magnificent brick-red fluorescence. The hydrochloride which appeared to be the best characterised salt, was prepared in the following way:—A concentrated solution of the base in ether was carefully dried over potassic carbonate and, after filtering, saturated with gaseous hydrogen chloride. In this way, the pure hydrochloride was precipitated as a deep-blue amorphous mass. This was rapidly collected, well washed with an ethereal solution of hydrogen chloride, and then allowed to stand in a desiccator partly filled with sticks of potash and partly with sulphuric acid in a vacuum until the excess of hydrochloric acid had been removed. A beautiful dark-bluish mass was thus obtained which had a magnificent coppery lustre, and outwardly resembled indigo in every respect.

The analyses gave the following result:—

- I. 0.2120 gram substance gave 0.1100 gram H_2O and 0.5390 gram CO_2 .
- II. 0.2012 gram substance gave 0.1057 gram H_2O and 0.5130 gram CO_2 .
- III. 0.2203 gram substance gave 11.5 c.c. N. $t = 21^\circ$. Bar. = 717 mm.
- IV. 0.2078 gram substance gave 0.1141 gram $AgCl$.
- V. 0.3795 gram substance gave 0.2160 gram $AgCl$.

	Found.				
	I.	II.	III.	IV.	V.
C.....	69.34	69.53	—	—	—
H.....	5.76	5.83	—	—	—
N.....	—	—	5.48	—	—
Cl.....	—	—	—	13.59	14.08

Theory. $C_{30}H_{30}N_2O_2Cl_2$.

C.....	69.09	per cent.
H.....	5.76	„
N.....	5.37	„
Cl	13.63	„
O.....	6.14	„

This salt has, therefore, the formula $C_{30}H_{30}N_2O_2Cl_2$. It dissolves in warm water, more easily in alcohol, forming beautiful indigo-blue solutions, which possess the magnificent brick-red fluorescence already described. It is remarkable that the solutions of this hydrochloride should show the same absorption-spectrum as indigo. If the solution in alcohol is warmed with zinc-dust and a little hydrochloric acid, the colour changes first to pink, and then entirely disappears. On filtering and shaking with air a beautiful crimson solution is produced which possesses a red fluorescence even more marked than that of the original substance, and reminds one strongly of magdala red.

If platinum chloride is added to the solution of the hydrochloride in alcohol, the platinumchloride is precipitated as a bluish-black amorphous mass which, after being collected, well washed with water, and dried over sulphuric acid in a vacuum, gave the following numbers on analysis:—

0.2536 gram of substance gave 0.0559 gram of platinum.

	Found.	Theory. $(C_{30}H_{30}N_2O_2Cl_2)PtCl_4$.
Pt.	22.04 per cent.	22.76 per cent.

This platinumchloride is sparingly soluble in water and alcohol. From the above results there can be but little doubt that the base of this colouring matter has the empirical formula $C_{10}H_{10}N_2O_2$, and is capable of forming salts such as $(C_{30}H_{28}N_2O_2)_2HCl$ with 2 mols. of the acid.

No clue as to the arrangement of the atoms in this complicated molecule has as yet been obtained, and the further examination has for the meantime been postponed until our knowledge of the trimethylene compounds is more developed.

The second base, produced by the action of hydroxylamine on benzoyltrimethylene, which is left behind after extracting the base $C_{30}H_{28}N_2O_2$ with ether, was then examined.

After washing well with water and drying over sulphuric acid in a vacuum, it presented exactly the appearance of amorphous phosphorus, and gave the following numbers on analysis:—

- I. 0.1453 gram substance gave 0.0707 gram H_2O and 0.4107 gram CO_2 .
- II. 0.1167 gram substance gave 0.0576 gram H_2O and 0.3362 gram CO_2 .
- III. 0.1321 gram substance gave 0.0630 gram H_2O and 0.3738 gram CO_2 .
- IV. 0.1470 gram substance gave 10.6 c.c. N. $t = 22^\circ$. Bar. = 716 mm.
- V. 0.2025 gram substance gave 14.5 c.c. N. $t = 20^\circ$. Bar. = 716 mm.

	Found.				
	I.	II.	III.	IV.	V.
C.....	77.08	77.17	77.17	—	—
H.....	5.41	5.48	5.29	—	—
N.....	—	—	—	7.68	7.73
Theory. (C ₁₁ H ₉ NO) _n .					
C.....	77.19 per cent.				
H.....	5.26 „				
N.....	8.18 „				
O.....	9.36 „				

Analyses I, II, and IV were done for the first sample, III and V from a preparation made later on. This base appears, therefore, to have the formula (C₁₁H₉NO)_n, perhaps C₃₃H₂₇N₃O₃.

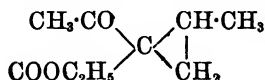
It is sparingly soluble in boiling alcohol, benzene, and toluene, but easily so in acetone, aniline, and nitrobenzene, forming reddish-brown solutions, from which it is precipitated in an amorphous condition on evaporation. All attempts to obtain it in a crystalline condition were unsuccessful.

It dissolves in alcoholic hydrochloric acid, producing a greenish-violet solution, which fluoresces in the same way as, although to a much less extent than, the salts of the base C₃₀H₂₃N₂O₂.

It dissolves in concentrated sulphuric acid with an intense olive-green colour; on diluting with water, a green amorphous mass is precipitated, which is perhaps the sulphate of the base.

ACTION OF PROPYLENE BROMIDE ON ETHYL ACETOACETATE.

Ethyl Acetylmethyltrimethylenecarboxylate (1, 2, 1),



It was next thought necessary, in order to prove whether the above method for the formation of trimethylene-derivatives was of general application, to try the action on ethyl acetoacetate of some other dibromide which was constituted similarly to ethylene bromide. For this purpose propylene bromide, CH₃·CHBr·CH₂Br, was selected, and the reaction carried out in the following way:—

4.6 grams of sodium were dissolved in 60 grams of absolute alcohol, and then a mixture of 26 grams of ethyl acetoacetate and 21 grams of propylene bromide were slowly poured in, the whole being well cooled during the operation.

This mixture, after being heated at 100° for 10 hours in a soda-

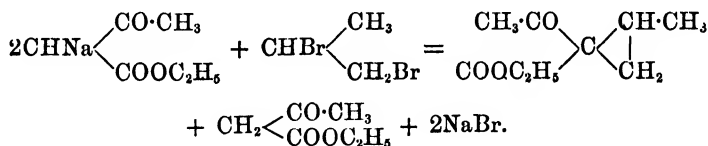
water bottle, had a neutral reaction, a sign that the reaction was finished. Water was then added, and the oily product several times extracted with ether, the ethereal solution dried over calcic chloride, and the ether distilled off. The residual oil was again heated at 100° for 10 hours with 2.3 grams of sodium (dissolved in 35 grams of absolute alcohol) and 12 grams of propylene bromide.

The product was isolated, as described before; and carefully fractionated, when, after a little unchanged propylene bromide had gone over, by far the greater quantity distilled between 180° and 230° , a thick blackish oil remaining in the retort. On repeatedly fractionating the portion $180-230^{\circ}$, it was at last obtained pure, as a colourless oil boiling at $215-217^{\circ}$ (720 mm.); it gave the following numbers on analysis:—

0.1813 gram substance gave 0.1375 gram H_2O and 0.4225 gram CO_2 .

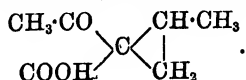
	Found.	Theory.
C	63.55 per cent.	63.53 per cent.
H	8.42 „	8.24 „
O	28.03 „	28.23 „

This substance was therefore ethyl acetylmethyltrimethylene-carboxylate (1, 2, 1), and is formed by the action of propylene bromide on ethyl acetoacetate, according to the following equation:—



It is a colourless faintly smelling oil, which boils at $215-217^{\circ}$ (720 mm.). On cooling down below -10° , it becomes very thick and appears inclined to crystallise. The yield is not good, a considerable quantity of high-boiling oils being formed at the same time.

Acetylmethyltrimethylenecarboxylic Acid (1, 2, 1),



In order to obtain this acid, the pure ether was mixed with excess of a moderately concentrated solution of alcoholic potash, and allowed to stand for about seven days at the ordinary temperature, at the end of which time the hydrolysis was nearly complete. The product was

then diluted with water and a trace of unchanged oil carefully removed by extraction with ether. On acidifying the solution of the potassic salt of the acid with dilute sulphuric acid, it became only slightly turbid, and no crystalline acid separated out. The whole was, therefore, several times extracted with pure ether, the ethereal solution well washed with water, in order to remove as much alcohol as possible, and then dried over calcic chloride. On distilling off the ether an almost colourless oily acid remained behind, which, on standing for some days over sulphuric acid in a vacuum, did not crystallise. In order to purify it, it was dissolved in a little dilute ammonia, well shaken with pure animal charcoal and filtered, a trace of colouring matter being thus almost entirely removed. On acidifying with dilute sulphuric acid and extracting with ether as before, a very thick almost colourless oil was obtained, which, after standing for some days over sulphuric acid in a vacuum in order to remove the last traces of ether, was analysed with the following result:—

0.2021 gram substance gave 0.1369 gram H_2O and 0.4347 gram CO_2 .

	Found.	Theory.
C	58.66 per cent.	$CH_3 \cdot CO \begin{array}{c} \diagup \\ \diagdown \end{array} \begin{array}{c} CH \cdot CH_3 \\ CH_2 \end{array}$ 59.15 per cent.
H	7.52 „	7.05 „
O	33.82 „	33.80 „

It was therefore acetylmethyltrimethylenecarboxylic acid (1, 2, 1). This acid does not appear to be decomposed by boiling with alcoholic potash. When heated in a test-tube, it is split up into carbonic anhydride and a low-boiling oil, which has the same peculiar odour as acetyltrimethylene. Unfortunately, owing to the small amount of material at my disposal, I was not able to purify and analyse it. It is probably acetylmethyltrimethylene (1, 2), $CH_3 \cdot CO \cdot CH \begin{array}{c} \diagup \\ \diagdown \end{array} \begin{array}{c} CH \cdot CH_3 \\ CH_2 \end{array}$.

Acetylmethyltrimethylenecarboxylic acid is fairly easily soluble in water, but less so than acetyltrimethylenecarboxylic acid.

The ammonium salt was prepared by dissolving the free acid in ammonia and allowing the excess of the latter to evaporate over sulphuric acid in a vacuum. On adding silver nitrate to the solution of this salt, the silver salt of the acid was precipitated as a white curdy mass slightly soluble in water. After collecting, washing well with water, and drying over sulphuric acid in a vacuum, the following results were obtained on analysis (see p. 855):—

Formula.	Name.	Melting point.	Boiling point (720 mm.) uncorr.	Boiling point of ethereal salt (720 mm.) uncorr.
$\begin{array}{c} \text{CH}_3 \\ \diagup \quad \diagdown \\ \text{CH}_2-\text{CH}_2 \end{array}$	Trimethylene.	Gas	—	Freund (<i>Monatsh. Chem.</i> , 1889, 622).
$\begin{array}{c} \text{CH}\cdot\text{COOH} \\ \diagup \quad \diagdown \\ \text{CH}_2-\text{CH}_2 \end{array}$	Trimethylenecarboxylic acid.	18—19°	182—184°	133—134°
$\begin{array}{c} \text{COOH}\cdot\text{C}\cdot\text{COOH} \\ \diagup \quad \diagdown \\ \text{CH}_2-\text{CH}_2 \end{array}$	Trimethylenedicarboxylic acid (1, 1).	140—141°	—	210°
$\begin{array}{c} \text{CH}\cdot\text{COOH} \\ \diagup \quad \diagdown \\ \text{CH}_2-\text{CH}\cdot\text{COOH} \end{array}$	Trimethylenedicarboxylic acid (1, 2).	137°	—	Conrad and Guthzeit (<i>Ber.</i> 17, 1185).
$\begin{array}{c} \text{COOH}\cdot\text{C}\cdot\text{COOH} \\ \diagup \quad \diagdown \\ \text{CH}_2-\text{CH}\cdot\text{COOH} \end{array}$	Trimethylenetricarboxylic acid (1, 1, 2).	184°	—	276° (760 mm.) Conrad and Guthzeit (<i>loc. cit.</i>).
$\begin{array}{c} \text{CH}\cdot\text{COOH} \\ \diagup \quad \diagdown \\ \text{COOH}\cdot\text{CH}-\text{CH}\cdot\text{COOH} \end{array}$	Trimethylenetricarboxylic acid (1, 2, 3).	145—150°	—	—
$\begin{array}{c} \text{COOH}\cdot\text{C}\cdot\text{COOH} \\ \diagup \quad \diagdown \\ \text{COOH}\cdot\text{CH}-\text{CH}\cdot\text{COOH} \end{array}$	Trimethylenetetracarboxylic acid (1, 1, 2, 3).	95—100°	—	245—247° (85 mm.).
$\begin{array}{c} \text{CH}_3 \\ \diagup \quad \diagdown \\ \text{CH}_3\cdot\text{CO}\cdot\text{CH} \end{array}$	Acetyltrimethylene.	Liquid.	112—113°	—

Formula.	Name.	Melting point.	Boiling point (720 mm.) uncorr.	Boiling point of ethereal salt (720 mm.) uncorr.
$C_6H_5 \cdot CO \cdot CH \begin{smallmatrix} CH_2 \\ \\ CH_2 \end{smallmatrix}$	Benzoyltrimethylene.	Liquid.	239—239.5°	—
$CH_3 \cdot CO \cdot C \cdot COOH \begin{smallmatrix} CH_2 \\ / \backslash \\ CH_2 \end{smallmatrix}$	Acetyltrimethylenecarboxylic acid (1, 1).	Liquid.	—	197—200°
$CH_3 \cdot CO \cdot C \cdot COOH \begin{smallmatrix} CH_2-CH_2 \\ \quad \end{smallmatrix}$	Benzoyltrimethylenecarboxylic acid (1, 1).	149—149°	—	280—283°
$CH_3 \cdot CO \cdot C \cdot COOH \begin{smallmatrix} CH_2 \\ / \backslash \\ CH_2-CH \cdot CH_3 \end{smallmatrix}$	Acetyltrimethylenecarboxylic acid (1, 2, 1).	Liquid.	—	215—217°
$C_6H_5 \cdot CNOH \cdot CH \begin{smallmatrix} CH_2 \\ \\ CH_2 \end{smallmatrix}$	Benzoyltrimethyleneoxime.	86—87°	—	—
$CH_2Br \cdot CH_2 \cdot CH \begin{smallmatrix} COOH \\ \\ COOH \end{smallmatrix}$	γ -Bromethylmalonic acid.	116—117°	—	—
$C_6H_5 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH_2Br$	ω -Bromopropyl phenyl ketone.	37—39°	—	—
$C_6H_5 \cdot CH_2 \cdot C \begin{smallmatrix} COOH \\ / \backslash \\ COOH \end{smallmatrix} \cdot CH_2 \cdot C_6H_5$	Dibenzylmalonic acid.	170—172°	—	—

Bases produced by the action of Hydroxylamine on Benzoyltrimethylene.

- I. $C_{30}H_{38}N_2O_2$
 II. $(C_{11}H_{13}NO)_2 = C_{22}H_{26}N_2O_3$ (?)
 Hydrochloride = $C_{30}H_{38}N_2O_2 \cdot 2HCl$.
 Platinochloride = $C_{30}H_{38}N_2O_2 \cdot H_2PtCl_6$

0.3112 gram substance gave 0.1339 gram silver.

	Found.	Theory. $C_7H_2O_3Ag$.
Ag.	43.02 per cent.	43.38 per cent.

It is evident, therefore, that the action of propylene bromide on ethyl acetoacetate is exactly similar to that of ethylene bromide, so that it is probable that this reaction for forming trimethylene-derivatives is a general one.

In conclusion, I append a table (pp. 853 and 854) of the compounds mentioned in this paper.

LXXIX.—*Action of Sodic Alcoholates on Ethereal Fumarates and Maleates.*

By T. PURDIE, Ph.D., B.Sc., Assoc. R.S.M., Professor of Chemistry in the University of St. Andrews.

IN a former communication to this Journal (Trans., 1881, 344), it was shown, that by the action of sodic alcoholates in alcoholic solution on the ethereal salts of fumaric acid, the elements of 1 mol. of alcohol are added to the ether; and that by saponification of the products of the action, an etheric acid is obtained, bearing the same relation to malic acid which the etheric acids of the formula



do to the acids of the lactic series. Thus by the action of sodic ethylate in ethylic alcohol on ethylic fumarate, and by the action of sodic isobutylate in butylic alcohol on isobutylic fumarate, ethoxy-succinic and isobutoxysuccinic acids are respectively obtained. The most probable explanation of the reaction seems to be, that by the addition of 1 mol. of sodic alcoholate to the fumaric ether, a sodium-derivative of the ethereal salt of the new acid is first formed, and that this intermediate product is decomposed by the free alcohol, sodium being replaced by hydrogen, and sodic alcoholate reproduced. The action in fact seems to be analogous to that which takes place when malic acid is produced by heating sodic fumarate with an aqueous solution of sodic hydrate. Whilst, however, the latter change is effected only after prolonged heating, the former takes place rapidly and with considerable evolution of heat.

In the present investigation, further experiments have been made with the view of elucidating the nature of the chemical change in question; the action has also been applied to the ethereal salts of maleic acid with the object of contributing to our still imperfect

knowledge of the nature of the isomerism of fumaric and maleic acids.

The experiments described furnish some new facts regarding the nature of the reactions concerned in the production of these bibasic etheric acids, and show that the addition products obtained from fumaric and maleic ethers are identical, or if not identical, that their isomerism is of the same kind as that of substances which differ only in crystallographic and optical properties.

In order to obtain evidence that the first stage in the reaction between sodic alcoholates and fumaric ethers is the formation of a sodium-derivative, attempts were made in various ways to cause alcoholic iodides to act on the supposed sodium compound, in the expectation that the higher homologues of etheric succinic acids would be formed. Experiments in this direction, however, have been so far unsuccessful, owing to the instability of the sodium compounds in the presence of alcohol, and to the formation of bye-products, when alcohol is excluded. Thus dry sodic ethylate was added in simple molecular proportion to ethylic fumarate, and the product of the reaction, a thick semi-solid mass, digested with methylic iodide, and then saponified. A lead salt was obtained from the product of the saponification, yielding by decomposition with sulphuretted hydrogen an acid which did not crystallise, but remained on drying in the form of a thick dark-coloured syrup. This substance contained no ethoxysuccinic acid, for its ammonium salt did not give the characteristic precipitate of calcic ethoxysuccinate on addition of calcic chloride. A silver salt, obtained approximately pure by the fractional precipitation of the ammonium salt, was analysed by combustion, and gave numbers which, though they led to no simple formula, indicated that a synthesis had taken place. In other experiments, in which a solution of ethylic fumarate in dry ether was used with the object of moderating the action of the alcoholate, attempts to obtain the products in a pure state were not more successful. The action of the alcoholates in the dry state was therefore not further investigated.

As the action of the methylate seemed to be attended with the production of less bye-product than that of the ethylate or isobutylate, the reaction between sodic methylate in alcoholic solution and ethylic fumarate was next examined.

Action of Sodic Methylate on Ethylic Fumarate.

In the first experiment described below, the ethylic fumarate used was made by heating the alcoholic solution of fumaric acid with sulphuric acid, but this method, it was afterwards found, is unsuitable for obtaining pure ethylic fumarate. By subjecting the ether pre-

pared by this method to fractional distillation, a considerable quantity of a substance was obtained from the higher fractions, which solidified on cooling in the form of crystalline scales of pearly lustre, and proved on analysis to be the hydric ethylic fumarate described by Laubenheimer :—

0·2437 gram of the substance gave 0·1268 gram H_2O and 0·4446 gram CO_2 .

	Calculated for $\text{C}_6\text{H}_8\text{O}_4$.	Found.
Carbon	50·00	49·76
Hydrogen	5·55	5·78
Oxygen	44·45	—
	<hr/> 100·00	

Ethylic fumarate was added to a solution of sodic methylate, formed by dissolving sodium in ten times its weight of methylic alcohol, the sodium used being in excess of the proportion of 1 atom of sodium to 1 mol. of ethereal salt. A considerable amount of heat was evolved by the action, but by adding the ether slowly and cooling, much less coloration was produced than in the reaction between sodic ethylate and ethylic fumarate. A heavy white precipitate was quickly thrown down, some more methylic alcohol was added, and after the mixture had stood for an hour, water was added, which dissolved the precipitate without causing the separation of oil. The alcohol was distilled off, and the residue heated with addition of potassic hydrate until the solution remained permanently alkaline. Neither on acidifying with hydrochloric acid, nor on boiling a test portion of the neutralised solution with baric chloride was any precipitate produced, showing that no fumaric acid was left unacted on. On boiling the neutral solution, however, with calcic chloride, a heavy crystalline precipitate gradually formed resembling calcic ethoxysuccinate in appearance and mode of precipitation. The salt was dried at 100° , and on combustion was found to be calcic methoxysuccinate :—

- I. 0·2271 gram gave 0·0739 gram H_2O and 0·2364 gram CO_2 ; the residue weighed 0·0966 gram and yielded 0·1636 gram CaSO_4 , and it contained therefore 0·0292 gram CO_2 .
- II. 0·2326 gram gave 0·0729 gram H_2O , 0·2369 gram CO_2 , and a residue weighing 0·1050 gram, yielding 0·1247 gram CaCO_3 , and containing therefore 0·0352 gram CO_2 .
- III. 0·3324 gram gave 0·1016 gram H_2O , 0·3278 gram CO_2 , and 0·1630 gram of residue, yielding 0·1780 gram CaCO_3 , and containing therefore 0·0633 gram CO_2 .

	Calculated for $C_5H_6CaO_5$.	Found.		
		I.	II.	III.
Carbon.....	32.26	31.90	31.90	32.09
Hydrogen.....	3.22	3.62	3.48	3.40
Calcium.....	21.51	21.19	21.44	21.42
Oxygen.....	43.01	—	—	—
	<hr/> 100.00			

A weighed quantity of the calcic salt was treated with rather less than the volume of decinormal solution of sulphuric acid required by calculation for its decomposition; the mixture was evaporated on the steam-bath, and the acid separated from the calcic sulphate by means of absolute alcohol. On evaporating the alcoholic solution, a syrup was left, which solidified to an opaque crystalline mass. The acid, after being powdered and pressed between filter-paper, was dissolved in ether, and filtered; on evaporating the ether, the residue was dissolved in water, and the solution filtered again. The water was then evaporated, and the residual syrup allowed to crystallise in a vacuum over sulphuric acid. The acid was found to melt at 101–103°, and the following results were obtained by combustion:—

0.2342 gram gave 0.1179 gram H_2O and 0.3482 gram CO_2 .

	Calculated for $C_5H_6O_5$.	Found.
Carbon	40.54	40.55
Hydrogen	5.41	5.59
Oxygen	54.05	—
	<hr/> 100.00	

Attempts to determine the nature of the white precipitate which was formed on adding the fumarate to the methylate were unsuccessful. It contained about 19 per cent. of sodium, and was probably a mixture of salts, the production of which was due to the presence of the monethylic fumarate already referred to. When dried in a vacuum, and heated with ethylic iodide in a closed tube at 100°, no sodium iodide was formed.

Throughout the rest of the investigation pure ethylic fumarate, prepared by the action of ethylic iodide on argentic fumarate, was used, but as the material thus procured is somewhat costly, the experiments were performed on a smaller scale than would have been otherwise desirable.

Preliminary experiments having shown that on adding pure ethylic fumarate to a solution of sodic methylate prepared from the anhydrous alcohol, a crystalline substance is thrown down which after-

wards dissolves again in the liquid, two or three drops of sodic methylate solution, prepared by dissolving sodium in ten times its weight of methylic alcohol, were added to 3 grams of ethylic fumarate diluted with 2 grams of methylic alcohol; the whole solidified at once to a crystalline mass with considerable evolution of heat and some coloration of the product. Water was at once added, and the crystals filtered off and thoroughly freed from adherent liquid by filter-paper; they were then dissolved in hot ether, and the solution separated by filtration from a slight residue. The crystals obtained by evaporation of the ether were dried in a vacuum. The substance fused at 102° , left no residue when heated on platinum foil, and was soluble in water and in methylic alcohol from which it crystallised in long needles. These properties are the same as those of methylic fumarate (*Ber.*, 12, 2282), and the substance was identified by the following analysis:—

0.2384 gram gave 0.1229 gram H_2O and 0.4376 gram CO_2 .

	Calculated for $C_6H_8O_4$.	Found.
Carbon	50.00	50.06
Hydrogen	5.56	5.73
Oxygen	44.44	—
	<hr/> 100.00	

The weight of methylic fumarate thus obtained from 3 grams ethylic fumarate was 1.2 grams; after a time, however, some more of the substance came out from the solution from which the main portion had been separated. This solution was saponified with sodic hydrate, acidified with hydrochloric acid, and allowed to stand, when very little fumaric acid separated, but on boiling the neutral solution with calcic chloride a considerable quantity of calcic methoxysuccinate was obtained.

Another experiment was made exactly as that just described, and with the same quantities of material, but the mixture of ethereal salt and alcoholate was allowed to stand a few minutes. The crystalline semi-solid product became partially liquid, only 0.3 gram of methylic fumarate was obtained, whilst an oil separated on evaporating off the methylic alcohol from the filtrate; this oil yielded an abundant precipitate of calcic methoxysuccinate on saponification, and only traces of fumaric acid.

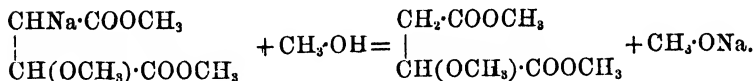
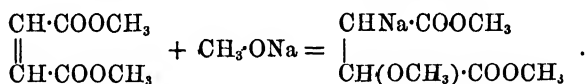
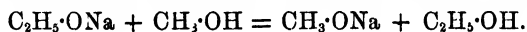
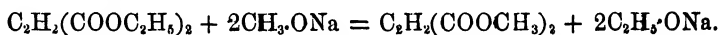
In a third experiment, 10 grams of ethylic fumarate were added gradually to sodic methylate solution containing 5 grams of sodium. The methylic fumarate which was formed on each addition of the ethylic salt dissolved almost immediately to a clear solution, which was poured into cold dilute sulphuric acid. The acid solution was

shaken up with ether several times; after removing the ether, neither fumaric acid, methoxysuccinic acid, nor other organic acid could be detected in the remaining liquid. The ethereal extract was dried with calcic chloride, and on distillation yielded an oil which boiled about 220° , but not without considerable loss from decomposition. The oil weighed about 8 grams, and did not contain fumarate. The quantity was too small to fractionate, but a combustion gave results approximating to the numbers required for methylic methoxysuccinate. This substance contains 6.82 per cent. of hydrogen and 47.73 per cent. of carbon; the numbers obtained by analysis were 7.05 and 46.24. The oil, which was insoluble in water, was readily saponified by sodic hydrate; the solution was acidified with hydrochloric acid, but no fumaric acid separated, whilst on neutralising and boiling with calcic chloride, the characteristic calcic methoxysuccinate was obtained.

In a fourth experiment, 10 grams of ethylic fumarate in 5 grams of methylic alcohol, and a quantity of sodic methylate containing about 0.3 gram sodium were used, the weight of sodium being thus less than a quarter of that required by calculation for 1 atom of sodium to 1 mol. of ethereal salt. The same phenomena were observed as before, but the methylic fumarate did not entirely dissolve even on heating on the water-bath; methylic alcohol was therefore added until all was dissolved, and the heating was continued, using a reflux condenser. For some time, the presence of methylic fumarate could be detected on evaporating some of the alcohol from a small test portion in a watch-glass, but after heating for about two hours, the crystalline methylic fumarate could no longer be observed; a slight amorphous precipitate had been formed, due probably to saponification. The whole product was poured into water, which it rendered only faintly alkaline. From this solution, the methylic methoxysuccinate was extracted with ether as before. The residual aqueous solution contained only traces of fumaric acid, and yielded 1 gram of dry calcic methoxysuccinate; the oil obtained from the ethereal extract after being heated to 115° , weighed 8 grams, and when saponified with potassic hydrate, gave 6.6 grams of calcium salt. When the solution was acidified before precipitation, no fumaric acid separated, but a crystalline salt was formed, readily soluble in excess of hydrochloric acid; this was found to be the acid potassium salt of methoxysuccinic acid: an analysis of this salt will be found below. Methoxysuccinic acid of melting point $101-103^{\circ}$ was obtained from the calcic salt as already described.

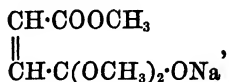
It will be seen from these experiments that the first change which takes place when sodic methylate acts on ethylic fumarate in presence of methylic alcohol, is the production of methylic fumarate by double

decomposition with evolution of heat; further, that the sodic methylate is able to produce much more than its equivalent molecular proportion of methylic fumarate, from which it appears that the sodium ethylate, which is produced by the double decomposition, is reconverted in the presence of an excess of methylic alcohol into sodic methylate, which acts on a fresh quantity of ethylic fumarate, until the greater part, if not the whole, of the latter is converted into methylic fumarate. The methylic fumarate, if left in contact with the methylic alcohol, is dissolved, and under the action of the sodic methylate, even in the cold, rapidly takes up the elements of 1 mol. of methylic alcohol, forming methylic methoxysuccinate. If the latter action be assisted by heat, a small quantity of sodic methylate will gradually convert a comparatively large quantity of fumarate into methoxysuccinate, little saponification taking place, and very little fumaric acid being left unacted on. It appears, therefore, that in this change also, as in the production of the methylic fumarate, the action of the sodic methylate is continuous. If a larger quantity of sodic methylate be used, as in the third experiment described, almost the whole of the ethylic fumarate is converted into methyl methoxysuccinate, even without the application of heat. The chemical reactions which take place may be expressed by the following equations:—



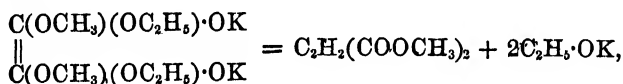
The experiments, it is true, afford no proof of the formation of a sodium compound at any time during the reaction, but the addition of the elements of 1 mol. of alcohol to the ether is explicable only on the assumption of the actual or potential existence of such a compound in the solution. Ethylic fumarate was heated in closed tubes at 100° with ethylic alcohol, but no addition product could be found.

We must conclude, therefore, either that the unstable sodium compound is actually formed and rapidly decomposed, or that nascent alcohol, so to speak, formed by the interaction of molecules of sodic methylate and methylic alcohol, is able to effect the addition though free alcohol cannot. The sodium compound formed may possibly be the derivative of an acid hydrol, represented by the formula—



which, by decomposition in the presence of alcohol, yields a saturated compound, but according to this supposition we should expect to get, as a final product, a sodic methylic salt, and not a normal ethereal salt, as is the case.

The interchange of alcoholic radicles between an ethereal salt and an alcohol effected in the manner described above, does not appear to have been observed hitherto. Salomon has described several chemical changes of a somewhat similar nature (*Ber.*, 8, 1506), as for instance, when potassic methylate acts on ethereal salts of thiocarbonic acids and on ethylic oxalate, but in all these cases the interchange is accompanied by partial saponification of the normal ether. Thus, when potassic methylate and methylic oxalate were made to react, potassic methylic oxalate was found to have been formed. The reaction may be represented by supposing (see Miller's *Elements of Chem.*, III, Sec. I, 923) that one of the COOC_2H_5 groups combines with the methylate, forming $\text{C}(\text{OCH}_3)(\text{OC}_2\text{H}_5)(\text{OK})$, which then probably reacts with the other COOC_2H_5 group, forming potassic methylic oxalate and ethylic ether. In order, however, to apply that method of representation to the present case, we must suppose that the potassoxyl group splits off entirely from the acid radicle, forming potassic ethylate according to the equation—



a change which seems rather anomalous. It is more probable that the interchange is effected simply by double decomposition, as has been already suggested, and this supposition is rendered the more probable considering the high *etherification velocity* of methylic, as compared with ethylic alcohol, whilst the heat of formation of sodic methylate differs but slightly from that of sodic ethylate (*Compt. rend.*, 101, 318). The conversion of ethylic into methylic fumarate is by no means an isolated instance of the kind of reaction under discussion. I have been for some time engaged with the investigation of the interchange of alcoholic radicles between the ethereal salts of other acids and alcohols, induced by the presence of various reagents, and being desirous of reserving the field of research, I append some of the results already obtained. It has been found that other substances besides the sodic derivatives of the carbinols are able to induce the change. The addition of potassic carbonate or baric hydrate to a mixture of ethylic fumarate and methylic

alcohol produces an immediate precipitate of the methylic salt, sodic carbonate, anhydrous borax, and calcic chloride, induce the change more slowly. When potassic carbonate is added to a mixture of ethylic oxalate and methylic alcohol, methylic oxalate is produced simultaneously with potassic methylic oxalate. Ethylic cinnamate is similarly converted into methylic cinnamate.

Properties of Methoxysuccinic Acid and its Salts.

Methoxysuccinic acid is readily soluble in alcohol, water and ether, and on evaporation of the solvent, it remains as a thick syrup which quickly solidifies to a soft, opaque, white, crystalline mass. The crystallisation proceeds from points on the surface of the syrup, forming circular patches, which with their fine radiating lines and concentric rings have somewhat the appearance, when seen in a thin layer on glass, of the section of a dicotyledonous stem. It melts at $101-103^{\circ}$, and when heated in an ignition tube it evaporates, probably forming an anhydride, and leaves only a slight residue. Baric chloride gives no precipitate with a solution of ammonic methoxysuccinate even on boiling, but calcic chloride gives a characteristic crystalline precipitate, which, unless the solution is very concentrated, forms only on boiling, and is then very sparingly soluble in water. The lead salt, in appearance and mode of precipitation, is extremely like plumbic ethoxysuccinate. When plumbic nitrate is added to a solution of ammonic methoxysuccinate, no precipitate is formed for some time; but on shaking or rubbing the sides of the vessel containing the solution with a glass rod, plumbic methoxysuccinate separates in the form of a dense crystalline precipitate. Besides the calcic salt, of which analyses have been already given, the following salts have been also examined.

Hydric Potassic Methoxysuccinate.—A portion of the acid dissolved in water was neutralised with potassic carbonate, and then to the solution another equal portion of acid was added. In a few hours the bottom of the vessel was covered with a crust of minute sparingly soluble crystals, which were dried on filter-paper and analysed. The crystals were heated to 175° without losing weight; the salt is, therefore, anhydrous.

0.4895 gram gave 0.2270 gram K_2SO_4 .

	Calculated for $C_6H_7KO_6$.	Found.
Potassium	21.01	20.82

Zincic Methoxysuccinate.—The aqueous solution of the acid was heated with zincic carbonate in excess, filtered, and allowed to eva-

porate spontaneously in the air. Under these conditions, the solution evaporates until it forms a thick syrup, in which hard rounded crystalline nodules gradually form composed of flat plates massed together. If the solution is evaporated on the water-bath, a viscid gum is left, which does not crystallise, but on being rubbed with a glass rod, solidifies to a white crystalline powder, sparingly soluble in water. The exact determination of the water of crystallisation is attended with difficulty, as the salt is extremely efflorescent, losing 10 to 15 per cent. of its weight when exposed to the air for a few hours; whilst the last portions of water are given off only at a temperature a little below that at which the substance undergoes decomposition. From the analyses quoted below, it appears to crystallise with 4 mols. H_2O , with 3 of which it parts at a temperature somewhat above 100° , whilst it does not become anhydrous until about 210° ; at about 220° it begins to decompose. Certain irregularities regarding the temperatures at which the water is given off, were observed and could not be accounted for. Thus, in Analyses I, III, IV, and V, the salt was found, when heated to 135° , to contain 1 mol. H_2O , very little loss of weight occurring between 100 and 135° , whilst in II the water lost at 100° amounted to considerably more than 3 mols., the total loss at 210° being, however, 4 mols., as in the other cases. The zinc was precipitated as carbonate, the filtrate being in each case tested with ammonium sulphide to ensure that the precipitation was complete.

I. 0.8286 gram, dried in filter-paper, lost at 135° 0.1561 gram.

II. 0.4842 gram, dried in filter-paper, lost at 210° 0.1212 gram, and gave 0.1401 gram ZnO .

III. 0.7674 gram, dried in filter-paper, lost at 135° 0.1400 gram; at 210° suffered an additional loss of 0.0482 gram, and gave 0.2192 gram ZnO .

IV. 0.3297 gram, dried at 135° , gave by combustion in oxygen 0.1096 gram H_2O , 0.3169 gram CO_2 , and 0.1151 gram ZnO .

V. 0.3468 gram, dried at 135° , lost at 210° 0.0265 gram, and the residue gave by combustion in oxygen 0.0831 gram H_2O , 0.3004 gram CO_2 , and 0.1118 gram ZnO .

Calculated on $\text{C}_6\text{H}_6\text{ZnO}_8 + 4\text{H}_2\text{O}$.		Found.		
		I.	II.	III.
$3\text{H}_2\text{O}$	19.08	18.84	—	18.24
$4\text{H}_2\text{O}$	25.44	—	25.03	—
Zinc	22.97	—	23.22	—

		Found.		
		III.	IV.	V.
Calculated on $C_5H_6ZnO_5 + H_2O$.				
H_2O	7·86	7·68	—	7·64
Carbon	26·20	—	26·21	—
Hydrogen	3·49	—	3·69	—
Zinc	28·39	28·04	28·00	—
Oxygen	41·92	—	—	—
<hr/> 100·00				

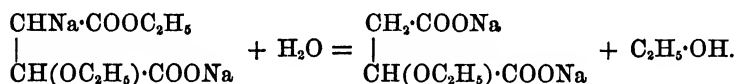
	Calculated on $C_5H_6ZnO_5$.	Found. V.
Carbon	28·44	28·14
Hydrogen	2·84	3·17
Zinc	30·81	30·82
Oxygen	37·91	—

It may be explained that Analyses IV and V were made on the same portion of substance which served for the estimation of water under I; also that the estimations of loss of water between 135° and 210° and of zinc given under III, are calculated on the substance dried at 135° , as it was found more easy to obtain the salt of constant composition when dried at that temperature than when dried on filter-paper. The salt loses water so readily, that it must be quickly dried with filter-paper, and it is difficult to remove adherent moisture without running the risk of efflorescence taking place. The estimations in II and III were made on portions of salt prepared separately. Considering the extremely efflorescent character of the salt, it is surprising that a portion of the water of crystallisation should be retained to such a high temperature as 210° . It must be admitted that the direct estimation of loss of water between 135° and 210° is not very trustworthy, as the substance begins to undergo decomposition at about 220° . On the other hand, the combustions, which were performed slowly in an abundant current of oxygen so as to avoid loss of zinc, and the direct estimations of zinc by precipitation, afford sufficient evidence that a molecule of water is retained when the salt is dried at 135° .

Action of Sodium Ethylate on Ethylic Fumarate.

The results of the investigation of this reaction and the properties of ethoxysuccinic acid have been already described in a previous communication. It was found that when the ingredients used were in the proportion of one atom of sodium to one molecule of ether, although some saponification took place, a large portion of the ethylic

fumarate was converted into ethylic ethoxysuccinate. Professor Wislicenus has informed me that he has observed in this reaction the same peculiarity of which mention has been already made in the case of the action of sodic methylate, namely, that a small quantity of the alcoholate will effect the addition of the alcohol to a comparatively large quantity of ethereal salt. Some more observations have been made with the view of further elucidating the nature of the reaction. When sodium is used in large excess, nearly the whole of the ethylic fumarate is converted, even without the aid of heat, into a sodium-derivative of ethoxysuccinic acid, which is gradually precipitated on standing. In two experiments, in which this compound was collected and washed with alcohol, 5.5 grams and 10 grams of dry substance were obtained respectively from 5 grams and 10 grams of ethylic fumarate. The compound is soluble in water with slight evolution of heat, producing an alkaline solution, which, on being heated, becomes neutral. No fumaric acid is precipitated on acidifying the solution with strong acid, but on boiling with calcic chloride, an abundant precipitate of calcic ethoxysuccinate is obtained. These reactions seem to indicate that a sodium-derivative, possibly sodic ethylic ethoxysodosuccinate, is formed, which is decomposed by water, with the formation of sodic ethoxysuccinate according to the equation—



Determinations of sodium in two separate preparations of the dry compound gave 19.22 and 18.87 per cent., the number required for sodic ethylic ethoxysodosuccinate being 19.66. Sodic ethoxysuccinate contains 22.33 per cent. of sodium; the numbers obtained from estimations of sodium in the substance prepared by treating the supposed sodium-derivative with water and drying the residue at 120°, were 19.41 and 19.78. I purpose making a further study of the nature of these compounds, as soon as I have material available for the purpose. By heating the sodium-derivative, if such it is, with alcoholic iodides, the homologues of the alkyloxysuccinic acids should be formed.

Ethoxysuccinic acid is an extremely stable substance. Whilst hydroxysuccinic acid—malic acid—when heated, parts readily with the elements of water, the etheric acid may be distilled without alcohol being split off. When heated to 150°, the acid loses weight, but very little decomposition takes place, the melting point of the residue being only 2° lower than that of the original acid. When distilled, an anhydride is probably produced; but it is evident from the fol-

lowing analysis of the product of distillation, that no further decomposition takes place, and that the acid is again reproduced on standing.

0.2433 gram gave 0.1267 gram H_2O and 0.4005 gram CO_2 .

	Calculated for $C_6H_{10}O_5$.	Found.
Carbon	44.45	44.89
Hydrogen	6.17	5.79
Oxygen	49.38	—
	<hr/> 100.00	

Descriptions and analyses of the calcium, barium, and silver salts have been already given (Trans., 1881, *loc. cit.*). The lead salt being characteristic, was also analysed for the purpose of comparing the acid with the corresponding compound obtained from maleic acid. On adding plumbic nitrate to a neutral solution of ammoniac ethoxysuccinate, the solution remains clear for some minutes; but on stirring it a dense crystalline precipitate of the anhydrous lead salt gradually forms. On heating the salt, previously dried in filter-paper, to 100° , no loss of weight occurred, and the following results were obtained by ignition and subsequent extraction with acetic acid:—

0.5295 gram salt yielded 0.2668 gram PbO and 0.0515 gram Pb .

	Calculated for $C_6H_5PbO_5$.	Found.
Lead	56.40	56.50

Action of Sodac Methylate on Ethylic Maleate.

Maleic anhydride was prepared by the method devised by Perkin (Trans., 1881, 561), namely, by the action of acetyl chloride on malic acid, the yield obtained being much the same as that quoted by Perkin. Thus 100 grams and 150 grams of maleic acid yielded respectively 46 grams and 70 grams of maleic anhydride. Ethylic maleate was prepared by acting on the silver salt with ethylic iodide according to Anschütz's method (*Ber.*, 12, 2280), the presence of free iodine being carefully avoided. A little of the ether was saponified and fumaric acid carefully tested for, but none was found. 10 grams ethylic maleate were added to 3 grams sodium dissolved in 30 grams methylic alcohol. The mixture became warm and slightly coloured, and a bulky precipitate was produced. On heating for some time, using a reflux condenser, saponification apparently took place, as much more precipitate was formed. The saponification in this case was probably due to the presence of water, as the alcohol had not been

carefully rectified. Water was then added—no oil separating—and the strongly alkaline solution was heated for some time. The methylic alcohol was boiled off, and fumaric acid tested for by acidifying a small portion with sulphuric acid; none was found. The neutralised solution gave no precipitate with baric chloride, but on adding calcic chloride and boiling, a calcium salt separated, which in appearance exactly resembled the calcic salt obtained in the corresponding reaction with ethylic fumarate, and on analysis was proved to have the same composition.

0.3528 gram gave 0.1080 gram H_2O , 0.3421 gram CO_2 , and 0.1755 gram residue, yielding 0.1888 gram CaCO_3 , and containing, therefore, 0.0698 gram CO_2 .

	Calculated for $\text{C}_6\text{H}_6\text{CaO}_6$.	Found.
Carbon	32.26	31.84
Hydrogen	3.22	3.40
Calcium	21.51	21.41
Oxygen	43.01	—
	<hr/> 100.00	

The acid was procured as before by decomposing the calcic salt with a little less than the calculated quantity of sulphuric acid, and extracting with alcohol. It formed a syrup which, on standing, solidified exactly like the methoxysuccinic acid obtained from fumaric acid, but it was slightly coloured, and was not obtained pure by successive solution in water and ether, the melting point, $95\text{--}100^\circ$, being less definite and some degrees lower than that of the methoxysuccinic acid prepared from the fumarate. Further efforts were not made to obtain it in the pure state from ethylic maleate, as it was afterwards found that a solution of maleic anhydride in alcohol could be substituted for the normal ether, and the acid was preferably prepared from this material.

Action of Sodid Ethylate on Ethylic Maleate.

The sodium used was somewhat in excess of that required by calculation for 2 atoms of sodium to 1 mol. of ethereal salt. In one experiment, the mixture was heated on the water-bath for a quarter of an hour, in another it was allowed to stand for some time without heating, but in neither case was any product obtained in a state fit for analysis. The phenomena attending the reaction were different from those observed in the case of ethylic fumarate and sodic ethylate. When the ethylic maleate was added to the solution of the ethylate, the mixture became quickly of a reddish-brown colour, heat

was evolved, and in the course of half an hour the liquid assumed a syrupy consistency, slight turbidity, but no precipitation being produced; even on heating there was only a slight precipitation. On heating the saponified product with calcic chloride as before, no precipitate formed until the solution was much concentrated, and the calcium salt bore no resemblance to calcic ethoxysuccinate, being readily soluble in water, and not so distinctly crystalline. Baric chloride produced but a slight precipitate; lead acetate and nitrate produced precipitates which were not at all like the characteristic crystalline lead ethoxysuccinate. Attempts to procure an acid in the pure state by decomposition of the lead salt and by extraction of the acidified solution with ether were equally unsuccessful; in both cases a dark-coloured uncrystallisable syrup inclosing some acicular crystals was obtained. The latter, as they were sparingly soluble in cold water, readily soluble in hot water, and sublimed without melting, were probably fumaric acid. If the reaction were moderated by cooling, and a smaller proportion of sodium used, a more satisfactory result would probably be obtained. I propose repeating the experiment with these modifications, as the reaction seems to differ in important respects from that which occurs with ethylic fumarate.

Action of Sodid Methylate on Hydric Methylic Maleate.

In order to avoid the preparation of the maleic ether, which is a troublesome as well as an expensive operation, the reaction under discussion was applied to a solution of maleic anhydride in methylic alcohol, in the hope that the acid ethereal salt, which would presumably be formed, might be capable of the same additive change as the normal ether. This was found to be the case.

Maleic anhydride was dissolved in its own weight of methylic alcohol, and the solution, after being boiled for some time with a reflux condenser and cooled, was added very gradually to the solution of sodium methylate, which was also kept cool; the proportion of materials used was somewhat in excess of 2 atoms of sodium to 1 mol. of anhydride, and the sodium was dissolved in twelve times its weight of methylic alcohol. When solutions prepared in this manner are mixed as above, evolution of heat and slight coloration of the liquid indicate that chemical action has taken place, but as long as the vessel is kept in cold water no precipitation occurs. When the mixture is no longer kept cool, it soon begins to become turbid, and a bulky white, partially crystalline precipitate gradually forms. Even after heating the mixture, it gives at first, when water is added, a strongly alkaline reaction, but on further heating the aqueous solution it becomes neutral. When the precipitate above referred to is filtered off from

the alcoholic liquor, freed from adherent sodium methylate by pressing between filter-paper and washing with a little methylic alcohol (if much alcohol is used the substance dissolves), and dissolved in water, it gives a strongly alkaline solution which becomes quickly neutral on boiling; this, on addition of calcic chloride, yields an abundant precipitate of calcic methoxysuccinate. It appears from these observations that the chemical changes which take place are probably as follows:—

When the maleic anhydride is heated with methylic alcohol, hydric methylic maleate is formed. On the addition of this ethereal salt to the sodic methylate, sodic methylic maleate, which is soluble in methylic alcohol, is produced, and when the temperature rises this compound adds on to itself the elements of 1 mol. of sodium methylate, forming sodic methylic methoxysodosuccinate; the latter substance, being less soluble in the alcohol, is precipitated, and when water is added to it sodium is exchanged for hydrogen with the production of sodic hydrate, which quickly effects complete saponification and leaves sodic methoxysuccinate.

The hydric methylic maleate, formed as above, is a syrupy liquid which does not crystallise on standing; if exposed to the air it deposits crystals of maleic acid. In order to test the supposed solubility of sodic methylic maleate in methylic alcohol, the solution of the acid ethereal salt in methylic alcohol was shaken up with ignited sodic carbonate and filtered; the filtrate, on evaporating the alcohol over sulphuric acid, deposited sodic methylic maleate as an indistinctly crystalline powder.

0.5847 gram of the salt yielded 0.2017 gram Na_2CO_3 .

	Calculated for $\text{C}_6\text{H}_6\text{NaO}_4$.	Found.
Sodium	15.13	14.97

An estimation of sodium in the supposed sodic methylic methoxysodosuccinate, obtained as already indicated, gave no satisfactory result, 23.54 per cent. being found instead of 22.33 per cent., as required by theory. The substance is excessively deliquescent, and partial saponification probably occurs during the process of washing with alcohol and drying. Some of the substance was dissolved in water, evaporated to dryness, and dried at 100° ; an estimation of the sodium showed that it had been thus converted into sodic methoxysuccinate.

0.4657 gram gave 0.2576 gram Na_2CO_3 .

	Calculated for $\text{C}_6\text{H}_6\text{Na}_2\text{O}_5$.	Found.
Sodium	23.96	24.00

In the main experiment made with the view of procuring the acid, no attempt was made to separate the sodium compound. After

heating the mixture for some time, water was simply added to the whole product of the reaction, and, after saponification, the calcium salt was thrown down, from which the acid was got as before. Both these substances were exactly like the corresponding compounds obtained from ethylic fumarate, but repeated analyses of the acid gave results for the carbon about 1 per cent. under the percentage required by theory for methoxysuccinic acid, and the melting point was 93—98°, whilst that of the corresponding acid from the fumarate had been found to be 101—103°. On the supposition that the acid was contaminated with maleic acid, a fresh quantity was prepared, particular care being taken to avoid the precipitation of calcium maleate. The solution from which the salt was to be precipitated was made up to half a litre, and the precipitate, after being filtered off, was redissolved with the aid of hydrochloric acid, and reprecipitated from a solution of the same bulk as before. 10 grams of maleic anhydride produced, in spite of the large loss unavoidably incurred by reprecipitation and thorough washing, 18·5 grams of pure calcium salt, being about 49 per cent. of the theoretical maximum yield. The following results were obtained by combustion of the salt dried at 100°:—

- I. 0·2560 gram gave 0·0798 gram H_2O , 0·2515 gram CO_2 , and 0·1236 gram residue, yielding 0·1363 gram $CaCO_3$, and containing, therefore, 0·0473 gram CO_2 .
- II. 0·2937 gram gave 0·0883 gram H_2O , 0·2779 gram CO_2 , and 0·1566 gram residue, yielding 0·1597 gram $CaCO_3$, and containing, therefore, 0·0672 gram CO_2 .

	Calculated for $C_5H_6CaO_5$.	Found.	
		I.	II.
Carbon	32·26	31·83	32·05
Hydrogen.... ..	3·22	3·46	3·34
Calcium	21·51	21·30	21·75
Oxygen.....	43·01	—	—
	<hr/> 100·00		

The acid was prepared from the salt as before, and was found to melt at 102—104°; its composition, as appears from the analysis below, agrees with that of methoxysuccinic acid.

0·2305 gram gave 0·1187 gram H_2O and 0·3439 gram CO_2 .

	Calculated for C_5H_6O	Found.
Carbon	40·54	40·69
Hydrogen	5·41	5·72
Oxygen	54·05	—

It is unnecessary to enumerate the properties of this acid, as they were found to be the same in all respects as those of the methoxysuccinic acid obtained from fumaric ether. Its melting point, like that of the latter, was not perfectly definite, and it was found to be about 1° higher; but this slight divergence was no doubt due to traces of impurity, as the acid in both cases had to be procured by solidification of the syrup, no solvent being found from which it would crystallise.

The calcic salt, of which analyses are given above, and the plumbic salt, resemble in appearance and mode of precipitation the calcic and plumbic methoxysuccinates obtained from ethylic fumarate; the baric salt also is soluble. For purposes of more exact comparison, the acid potassium, and zinc salts, were prepared.

Hydric Potassic Methoxysuccinate.—This substance was prepared as before; it was found to be anhydrous and to be unaltered at a temperature of 175° , as was the case with the salt obtained from ethylic fumarate. The results given below were obtained by combustion.

0.3225 gram gave 0.1156 gram H_2O , 0.3437 gram CO_2 , and 0.1183 gram K_2CO_3 .

	Calculated for $C_5H_7KO_5$.	Found.
Carbon.....	32.24	32.25
Hydrogen	3.76	3.98
Potassium	21.01	20.76
Oxygen	42.99	—
	<hr/> 100.00	

Zincic Methoxysuccinate.—This salt was prepared in the same manner as before. It will be seen from the estimations of water of crystallisation and of zinc which are given below, that the salt has the same constitution as the corresponding substance obtained from ethylic fumarate. It loses 3 mols. H_2O at 100° , or at a temperature slightly higher; at 135° it still retains 1 mol., with which it parts at a temperature only a little below that at which decomposition begins. The difficulty in getting correct estimations of the water of crystallisation was the same as that previously encountered (p. 864).

- I. 0.3323 gram dried in filter-paper lost 0.0626 gram at 135° .
- II. 0.8812 " " " 0.1739 "
- III. 0.2697 gram dried at 135° lost 0.0212 gram at 220° .
- IV. 0.3083 gram dried at 135° lost 0.0258 gram at 220° , and gave 0.1085 gram ZnO .
- V. 0.5502 gram dried at 135° gave 0.1955 gram ZnO .
- VI. 0.7073 " " " 0.2447 "
- VII. 0.7812 " " " 0.2728 " "

		Found.			
		Calculated for $C_6H_6ZnO_6 + 4H_2O$.		I.	II.
$3H_2O$	19.08			18.84	19.73

		Found.				
		III.	IV.	V.	VI.	VII.
		Calculated for $C_6H_6ZnO_6 + H_2O$.				
H_2O	7.86	7.86	8.37	—	—	—
Zinc	28.39	—	28.24	28.51	27.76	28.02

In spite of the close resemblance between the zincic methoxysuccinates obtained from the two separate sources, certain differences in the behaviour of the salts were observed, which seem to indicate that they are not identical. It will be seen that the salt obtained from ethylic fumarate is anhydrous at 210° , whilst that from ethylic maleate has to be heated 10° higher before it parts with all its water of crystallisation. Besides the estimations which are quoted above, experiments were made by heating portions of the two substances in watch-glasses placed close together in the same oven. The results as regards the exact temperatures at which the water is eliminated, and at which decomposition sets in, were not quite concordant, but in each case the salt from ethylic maleate had to be heated to a higher temperature than that from ethylic fumarate, before the changes in question occurred. Other differences also were observed, which could scarcely be attributed to traces of impurity in the substance. Thus the solution of the salt from ethylic fumarate, when left to evaporate spontaneously, assumes the form of a viscid syrup or gum before it crystallises, and the crystals, examined under the microscope, have the form of six-sided plates, whilst the solution of the salt from ethylic maleate, under similar conditions, though it becomes somewhat syrupy, crystallises without becoming of such a viscid consistence, and the individual crystals are for the most part prisms often arranged in a radiate fashion. In some cases this salt separated partly in crystals, partly in the form of a fine powder, before the solution attained the consistence of a syrup at all. The crystals obtained in both cases were too small for measurement.

Action of Sodio Ethylate on Hydric Ethylic Maleate.

In order to confirm the identity of the etheric acids obtained from fumaric and maleic acids, it seemed desirable to prepare ethoxy-succinic acid from maleic acid by the method just described for the preparation of the methoxy-acid, more particularly so as the action of sodio ethylate on normal ethylic maleate had failed to yield the acid in question.

The experiment was conducted as already described; the ingredients were used in the same proportion as in the preparation of methoxysuccinic acid, absolute ethylic being substituted for methylic alcohol. The ethylate seems to act more rapidly than the methylate. If the ethereal salt is added to the alcoholate, precipitation of a sodium-derivative takes place at once; if, however, the alcoholate is added in small quantities at a time to the ether, the solution remains clear until the mixture is nearly completed, a few minutes after which the whole becomes a semi-solid mass. From the product of the action, a sparingly soluble calcic salt was obtained, and from this the acid was prepared by decomposition with sulphuric acid and extraction with alcohol. 28 grams of maleic anhydride yielded 32 grams of calcium salt. The properties of this salt and of the acid were the same as those of the corresponding compounds obtained from fumaric acid, the only difference observed being that the melting point of the acid ($84-86^{\circ}$) was not quite so well defined as that of the acid prepared from fumaric acid which melts at 86° . Analyses of both the salt and the acid indicated the presence of some impurity, estimations of carbon in repeated combustions being lower than could be accounted for by the usual errors of analysis. The salt was therefore reprecipitated; estimations of calcium, as quoted below (I, II, and III), agreed closely with the calculated percentages, but the acid prepared from this salt still gave unsatisfactory results for carbon. It was again converted into the calcic salt, by combustion of which the results given below (IV) were obtained:—

- I. 0.2777 gram gave 0.1400 gram CaCO_3 .
 II. 0.3286 " 0.1663 "
 III. 0.3164 " 0.1592 "
 IV. 0.2677 " 0.0998 gram H_2O , 0.2949 gram CO_2 , and
 0.1336 gram residue, yielding 0.1349 gram CaCO_3 , contain-
 ing therefore 0.0581 gram CO_2 .

	Calculated for $\text{C}_6\text{H}_8\text{CaO}_5$.	Found.			
		I.	II.	III.	IV.
Carbon	36.00	—	—	—	35.96
Hydrogen . .	4.00	—	—	—	4.14
Calcium . . .	20.00	20.17	20.24	20.13	20.16
Oxygen	40.00	—	—	—	—

The acid prepared from the pure calcium salt showed the same melting point as before, namely, $84-86^{\circ}$, and still yielded low results for carbon, as will be seen from the following combustions:—

- I. 0.2290 gram gave 0.1312 gram H_2O and 0.3682 gram CO_2 .
 II. 0.2006 " 0.1143 " " 0.3229 "
 III. 0.2048 " 0.1144 " " 0.3297 "

	Calculated for $C_6H_{10}O_5$.	Found.		
		I.	II.	III.
Carbon.....	44.45	43.85	43.90	43.91
Hydrogen	6.17	6.37	6.33	6.20
Oxygen	49.38	—	—	—
<hr/>				
100.00				

In preparing ethoxysuccinic acid from ethylic fumarate, it was procured by decomposition of the lead salt with sulphuretted hydrogen. This method would probably have yielded a purer product in the present case, but as the various data concerning the acid itself, as well as its salts which are enumerated below, leave no doubt of its identity with the acid prepared from ethylic fumarate, it was thought unnecessary to undertake the further purification of the substance.

Ethoxysuccinic acid, prepared from hydric ethylic maleate, is very soluble in water, alcohol, and ether, and on evaporating the solvent, it is left in the form of a syrup, which on standing over sulphuric acid solidifies slowly to a transparent anhydrous crystalline mass. It melts at $84-86^\circ$, and after being heated to 150° and allowed to solidify again, the melting point is little altered. When calcic chloride is added to a soluble ethoxysuccinate, unless the solution is very concentrated, no precipitation takes place until the liquid is boiled, when the calcic salt separates in the form of a sparingly soluble crystalline powder. The baric salt is readily soluble in water. The lead salt is less readily precipitated by plumbic acetate than by plumbic nitrate; on addition of the latter reagent to a solution of ammoniac ethoxysuccinate, precipitation does not take place until the solution is well shaken or stirred; the anhydrous salt then separates as a dense crystalline powder. As the baric and plumbic salts are characteristic, they were subjected to analysis.

Baric Ethoxysuccinate.—This salt was prepared by neutralising an aqueous solution of the acid with baric hydrate, and allowing the liquid to evaporate spontaneously. As an analysis of the salt gave a rather low result for carbon, it was redissolved, and the solution allowed to evaporate until a portion of the salt had separated. The liquid was filtered, and the residue left by the spontaneous evaporation of the filtrate was used for the analysis, the particulars of which are given below. The salt prepared in this manner is a crystalline powder of a silky lustre, consisting of microscopic prisms which contain apparently one molecular proportion of water. An exact determination of the water of crystallisation is attended with difficulty, as it is given off partly on drying over sulphuric acid, but completely only when the substance is heated to about 160° . The salt being

hygroscopic, it cannot be weighed in the air-dried condition. The number calculated for 1 mol. H_2O is 5.71 per cent.; the percentage found was 6.45. The salt, dried at 160°C ., gave by combustion the following results:—

- I. 0.2842 gram gave 0.0729 gram H_2O , 0.2072 gram CO_2 , and 0.1886 gram BaCO_3 .
 II. 0.3206 gram gave 0.0813 gram H_2O , 0.2390 gram CO_2 , and 0.2121 gram BaCO_3 .

	Calculated for $\text{C}_6\text{H}_8\text{BaO}_5$.	Found.	
		I.	II.
Carbon	24.24	23.92	24.36
Hydrogen	2.69	2.85	2.82
Barium	46.13	46.15	46.01
Oxygen	26.94	—	—
	<hr/> 100.00		

Plumbic Ethoxysuccinate.—This salt was prepared by adding plumbic nitrate to a neutral solution of the ammoniac salt. It was dried in filter-paper, and did not lose weight on heating to 100° . By ignition and subsequent extraction with acetic acid, the following analytical results were obtained:—

1.1630 grams gave 0.2900 gram PbO and 0.3872 gram Pb .

	Calculated for $\text{C}_6\text{H}_8\text{PbO}_5$.	Found.
Lead	56.40	56.43

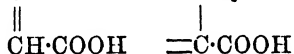
The various properties of ethoxysuccinic acid and its salts, which have been described, agree with those of the corresponding substance obtained from fumaric ether (Trans., 1881, 352).

Besides the cases of fumaric and maleic ethers, which have been discussed in this communication, we are acquainted with various instances of the conversion of an unsaturated into a saturated compound by the addition of the elements of a molecule of alcohol. A. Rinne (*Ber.*, 6, 389) observed that in the preparation of allylic cyanide a compound of this substance with alcohol was formed, which A. Pinner (*Ber.*, 12, 2053) has shown to be ethoxybutyronitrile. Since the publication of my first communication, Claisen and Crisner (*Annalen*, 218, 141) have found that by the saponification of ethylic benzalmalonate with alcoholic potash, potassic ethoxybenzylmalonate is formed, and K. Grosner has recently (*Inaug. Diss.*, Würzburg, 1885) applied the reaction to the ethers of the pyrocitric acids, and obtained from them ethoxypropanedicarboxylic acids. Probably the ethereal salts of many other monobasic and bibasic unsaturated acids

will be found capable of the same reaction. It may be mentioned that attempts to obtain etheric acids by heating the potassic salts of fumaric and maleic acids with sodic alcoholates were unsuccessful.

From the descriptions of the alkyloxysuccinic acids and their salts, prepared from fumaric and maleic ethers, it will be seen that the only compounds obtained from the two sources in which any difference of properties has been observed are the zinc salts of the methoxysuccinic acids. These differences may possibly be due to the presence of impurities in one or both of the substances, but they are more probably attributable to actual difference of constitution. It may be concluded that the additive compounds in question are either absolutely identical, or if not identical, then their relation to each other is of the same kind as the relation of certain of the malic and tartaric acids to one another. We may also conclude that this identity or close resemblance is a result of the constitutional relations of maleic and fumaric acids, and is not to be attributed to the conversion of the former into the latter substance during the progress of the reaction, as the chemical change takes place at ordinary temperatures and in alkaline solution.

The result obtained from the experiments is such as might be expected, reasoning from analogy. Accepting provisionally Fittig's formulæ, $\text{CH}\cdot\text{COOH}$ and $\text{CH}_2\cdot\text{COOH}$ for fumaric and maleic acid as



best representing the chemical reactions of which these substances are capable, it is evident that the compounds obtained from them by the addition of the elements of a molecule of alcohol should be chemically identical. On the other hand, it is by no means improbable that the acids so obtained might differ in optical and crystallographic characters, and that slight differences might be found in their salts, such as seem to exist in the methoxysuccinates of zinc. This is rendered the more probable in view of the interesting discovery of Kekulé and Anschütz (*Ber.*, 14, 717) that fumaric and maleic acids when oxidised yield respectively racemic and mesotartaric acids, and in view of the hypothesis advanced by these authors, that fumaric acid probably consists of dextro- and lævo-maleic acids.

Considering the parallelism which has been found to exist between the reactions of fumaric and maleic acids on the one hand, and mesaconic and citraconic acids respectively on the other, the results obtained by K. Grosner, already alluded to, are remarkable and interesting. He finds that ethylic citraconate and ethylic mesaconate, unlike ethylic maleate and fumarate, yield essentially different ethoxypropane-dicarboxylic acids, and that ethylic mesaconate and itaconate yield the same acid.

I purpose subjecting the salts of the etheric succinic acids, prepared from fumaric and maleic acids, to a more thorough examination, with the object more particularly of determining whether the additive products from fumaric acid are capable of being resolved into two optically active substances, as may probably be the case should the hypothesis of Kekulé and Anschütz be correct. I propose also to bring the etheric acid, prepared direct from malic acid and by other methods, within the scope of the investigation, as it will be a matter of interest to compare the alkyloxysuccinic acids from different sources with the different malic acids which Anschütz (*Ber.*, **18**, 1949) has now under investigation. I am desirous also of reserving for further study the various sodium-derivatives, which appear to be formed by the action of sodium alcoholates on fumaric and maleic ethers.

The results obtained in the preceding investigation may be summed up as follows:—

1. Sodic methylate dissolved in methylic alcohol acts *continuously* on ethylic fumarate, producing methylic fumarate, and ultimately methylic methoxysuccinate, an intermediate compound, methylic sodomethoxysuccinate, probably being formed. By saponification, methoxysuccinic acid is produced.

2. By the action of an alcoholic solution of sodium ethylate on ethylic fumarate, the latter is converted into ethylic ethoxysuccinate, or into a compound which is probably sodic ethylic ethoxysodosuccinate, according to the conditions of the experiment. Both compounds yield by saponification ethoxysuccinic acid.

3. By the action of sodium methylate on ethylic maleate or on hydric methylic maleate, methoxysuccinic acid is obtained; in the latter case a compound, probably sodic methoxysodosuccinate, being formed, which on treatment with water yields sodic methoxysuccinate.

4. By the action of sodic ethylate on hydric ethylic maleate, ethoxysuccinic acid is obtained.

5. The corresponding etheric acids formed from fumaric and maleic acids by the addition of the elements of a molecule of alcohol are identical, or, if not identical, their relation to each other is that of isomerides which differ only in crystallographic and optical characters.

LXXX.—Contributions to the Chemistry of the Cerite Metals. III.

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Introductory Remarks.

In a paper published several years ago (*Chem. Soc. J.*, Trans., 1882, 68, and *in extenso*, *Monatsh. Chem.*, 1882, 1—60), I endeavoured to determine the position of the cerite metals in the periodic system of elements, and arranged them in the order—

La ^{III} .	Ce ^{IV} .	Di ^{III-V} .
139	141·6	146·6

A little later (*Monatsh. Chem.*, 1882, 486, and Trans., 1883, 278), I succeeded in proving that the didymium from cerite is a *mixture*, and that the atomic weight of the true didymium is at most Di = 145·4. For lanthanum I found at the same time the number La = 138·28. Working with a more abundant supply of the rare material, Cleve, whilst confirming my number for lanthanum, that is, 138·28 (*Bull. Soc. Chim.*, **39**, 151, 289), found didymium to be Di = 142·3—142·4. If, as has hitherto been the case, the number found for the atomic weight of cerium by Bührig (*J. pr. Chem.* **120**, 222), namely, Ce = 141·6, be admitted to represent the truth, the order of the atomic weights of the said elements in the system would be as follows:—

	La.	Ce.	Di.
	138·2	141·6	142·3
Difference. . . .	3·4		0·7

It must be admitted that the lanthanum and didymium preparations with which Cleve determined the atomic weights of these elements were pure and homogeneous, and, as the method used by him does not involve any apparent source of error, we are justified in regarding his numbers as very nearly representing the truth. It is, however, very evident that the difference between the atomic weights of lanthanum and cerium (3·4) is much larger than that between cerium and didymium (0·7), and the question therefore arose whether Bührig's number (Ce = 141·6) is really the atomic weight of cerium, as is generally believed, especially as Wolf (*Sill. Amer. J.* [2], **46**, 53—62) has found the atomic weight of the *purest* cerium to be Ce = 137,

a much lower number than Bührig's. The object of the present investigation is to answer this question.

Historical Review.

Since 1816, the atomic weight of cerium has been determined by many chemists, but the numbers found, especially those which seem to be the most trustworthy, differ more widely from each other than might be expected. The following is a short review of the determinations made. For details I must refer partly to the original papers, partly to the works recently published by G. F. Becker (*Constants of Nature*, Part IV, Washington, 1880); F. W. Clarke (*Constants of Nature*, Part V, Washington, 1882); Lothar Meyer and Seubert (*Die Atomgewichte der Elemente*, Leipzig, 1883); and by Ostwald (*Lehrbuch der Allgemeinen Chemie*, Leipzig, 1884). My comments on the individual determinations form a special chapter of the present paper.

I should state that I call the oxide Ce_2O_3 and its salts *cerous*, and the oxide CeO_2 *ceric* and *not* cerium peroxide, as is done by some chemists, as the latter name must be reserved for the oxide CeO_3 , recently investigated by L. de Boisbaudran (*Compt. rend.*, **100**, 605), and Cleve (*Bull. Soc. Chim.*, **43**, 53). The numbers below refer to $\text{O} = 16$.

The number to be deduced from Hisinger's (*Schweig.*, **17**, 424; *Pogg. Ann.*, **8**, 186) experiments, made in 1814–16, is $\text{Ce} = 137.9$. The method is not given, and his cerium was contaminated with lanthanum and didymium, the existence of the last two elements not being known at that time.

Berlinger's (*Annalen*, **42**, 134) cerium salts were also rose-coloured. The numbers obtained by him were $\text{Ce} = 142.3$ from the relation of ceric oxide to silver chloride; $\text{Ce} = 142.3$ from that of ceric oxide to barium sulphate; and $\text{Ce} = 141.6$ from the combustion of cerous formate.

Rammelsberg's (*Pogg. Ann.*, **55**, 65) analysis of anhydrous cerous sulphate, made in 1842, gives $\text{Ce} = 134.3$.

Hermann (*J. pr. Chem.*, **30**, 184) in 1843, determined the relation of anhydrous cerous sulphate to barium sulphate. His numbers give $\text{Ce} = 139.4$.

From Marignac's (*Ann. Chim. Phys.* [3], **27**, 209; *Arch. Sci. Ph. Nat.* [1], **8**, 273) volumetric analysis of cerous sulphate solutions by means of barium chloride, it follows that $\text{Ce} = 141.8$; whilst the relation of anhydrous cerous sulphate to barium sulphate, Ce is 141.6. Later on (*Ann. Chim. Phys.* [3], **38**, 148), the same chemist gave the preference to the number $\text{Ce} = 137.7$, but without giving any experimental evidence.

Jegel, in 1858 (*Annalen*, **105**, 45), deduced the number $Ce = 1381$, from the combustion of cerous oxalate. An analysis of the sulphate gave $Ce = 137.8$. In both cases, the ceric oxide was analysed iodometrically.

Lothar Meyer and Seubert calculate, instead of the above numbers, $Ce = 137.4$ and 138.3 .

A combustion of the oxalate, made by Rammelsberg (*Pogg. Ann.*, **108**, 44) in 1859, gave $Ce = 138.1$.

All the above determinations were made with cerium preparations containing larger or smaller quantities of foreign earths, for the ceric oxide obtained was more or less brown coloured. In 1867, an extended investigation of the subject was undertaken by C. Wolf (*loc. cit.*) in Bunsen's laboratory, but unfortunately, it remained unfinished in consequence of his premature death, and has, up to the present, never been again taken up. The following details from Wolf's diary, published after his death by Genth, may be given here, as being important in relation to the present question.

Ceric nitrate prepared from the crude oxides, was decomposed by pouring its aqueous solution into boiling water containing some sulphuric acid, and the precipitate of basic nitrate and sulphate, N, was converted into cerous sulphate. This was recrystallised at least ten times. Wolf heated the sulphate over a small flame in a double platinum crucible, in order to determine the amount of water of crystallisation (by loss of weight), and from the aqueous solution of the anhydrous sulphate thus obtained the oxalate was precipitated by a boiling concentrated solution of oxalic acid. This, by careful ignition, was converted into ceric oxide. In the filtrate, the sulphuric acid was determined as barium sulphate. The excess of oxygen in CeO_2 (Ce_2O_4) over Ce_2O_3 was determined iodometrically. From these four data (H_2O , CeO_2 , Ce_2O_3 , and SO_3) the composition of the anhydrous cerous sulphate was first calculated, and from this the equivalent of cerium.

As the ceric oxide obtained in the first series of determinations had a brownish colour, part of the precipitate N was purified by dissolving and precipitating with boiling water; and in this way the precipitate N_x was obtained. The sulphate obtained from it gave a much paler ceric oxide.

The precipitates N_β , N_γ , and N_δ were obtained by Wolf in the same way, and the colour of the oxide was in each case paler than in the preceding. Wolf calls the oxide from N_γ almost white, and that from N_δ white.

It is a very remarkable circumstance that, after every purification, as the oxide became more nearly white, the equivalent of cerium was found to decrease.

In Wolf's original paper the following numbers are calculated for the equivalent of cerium:—

I.	II.	IV.	V.
46·187	45·760	45·699	45·664

This multiplied by 3 would represent the atomic weight as—

I.	II.	IV.	V.
138·561	137·280	137·097	136·992

If, according to Clarke, the atomic weight be calculated from the relation of $\text{Ce}_2(\text{SO}_4)_3$ to 2CeO_2 , as involving the least experimental error, the following numbers will be obtained (for $\text{O} = 16$, $\text{S} = 32\cdot06$):—

I.	II.	IV.	V.
$\text{Ce} = 139\cdot64$	138·27	138·04	138·00

From these experiments Wolf concluded that the remarkable diminution of the atomic weight of cerium could not be due to the elimination of didymium only, but that the first portions may have contained a foreign substance.

Wing (*Sill. Amer. J.* [2], 49, 358), in 1870, repeated Wolf's experiments and process of purification, without, however, going further, and his purest material gave $\text{Ce} = 137\cdot85$. From Wolf's and Wing's experiments Clarke calculates as a mean $\text{Ce} = 138\cdot039$.

Bühlig's (*loc. cit.*) experiments made in 1875, with a material free from didymium, in which large quantities of cerous oxalate were analysed by combustion in a current of oxygen, gave a remarkably high number, namely $\text{Ce} = 141\cdot523$ (Clarke). His ceric oxide varied from yellow to salmon colour. Later on I shall return to the objections which he raised against the analysis of cerous sulphate.

While my present investigation, which has occupied me for some time past, was in progress, H. Robinson (*Proc. Roy. Soc.*, 37, 150) published his paper on the same subject. The purification of his cerium salts was effected by Gibbs's method. The cerium solution, free from didymium, finally obtained, was precipitated with oxalic acid, and the air-dried oxalate was converted into the chloride by heating it in a current of hydrogen chloride. The cerous chloride, free from water and hydrogen chloride, was analysed volumetrically with a silver solution, according to Stas' method. As a mean of the results of seven experiments (reduced to a vacuum), Robinson found—

$$\text{Ce} = 140\cdot2593 (\text{O} = 16) \text{ or } \text{Ce} = 139\cdot9035 (\text{H} = 1).$$

This number, as I shall show later on, is to be considered exact, for

in the method used by Robinson, all possible experimental errors are reduced to a minimum; but I have nevertheless continued my experiments for several reasons. Firstly, the method I have used is different from that adopted by Robinson, and our experiments therefore mutually control each other. Secondly, Wolf's experiments challenge investigation as regards the *homogeneous* character of the material, and as Robinson did not touch this question, it was all the more necessary for me to devote my attention to it. Experience has shown, especially in the case of the rare earth metals, that the atomic weights, determined even by the most trustworthy methods, may differ by *several units* from the truth, if the material used consisted of a *mixture* of earths. The history of scandium, yttrium, didymium, and erbium may be quoted as examples.

Method of Investigation.

In the operations of dissolving, evaporating, and boiling, only such vessels were used as had been treated for some time beforehand with acids.

The acids, viz., hydrochloric, nitric, and sulphuric, were distilled shortly before use from a platinum retort, and kept in well-stopped bottles of Bohemian glass. A platinum tube, 60 cm. in length, 2.5 cm. wide, and weighing 600 grams, was used as a condenser, and for this I am much indebted to the Royal Society for a grant from the Government Grant Fund. Distilled water was once redistilled by means of the same arrangement, and absolute alcohol was similarly treated, the first and last portions of the distillate being rejected. The filter-paper used was kept in contact with warm hydrochloric acid for some time, and then well washed. In weighing, a fine balance, made by Verbeeck and Peckholdt, of Dresden, was used. In order to prevent the very sensible effect of radiant heat during weighing, the balance was covered on all sides with thick flannel, so that only the scale could be seen. To make the scale more visible, light was reflected upon it from the sides by mirrors, and at night the light of distant gas flames was concentrated upon it by lenses. If the method of vibrations be used in weighing, and the observation of the "point of rest" be often repeated, the weight of a body weighing about 50 grams may be determined accurately within 0.00001 to 0.00003 gram. The platinum crucibles were weighed in small thin glass bottles, and a similar vessel with platinum was used as counterpoise. As the weight of substance used was generally about 2 grams, rarely 5 grams, only a few small weights were used: in this way the errors of weighing were reduced to a minimum. The following was the true weight of the pieces used:—

2 = 2.00006	0.5 = 0.49978	0.05 = 0.04996
1 = 0.99996	0.2 = 0.19992	0.02 = 0.02012
1' = 0.99996	0.1 = 0.10001	0.01 = 0.01010
1'' = 1.00005	0.1' = 0.10001	0.01' = 0.01012
		rider = 0.01002

The weighings were reduced to a vacuum. In the balance case was placed a Klinkerfues' hygrometer with a thermometer. As a rule, this indicated about 35 per cent. of humidity. The thermometer stood almost always at 18°, and the mean height of the barometer was 742 mm.; as the deviations were such as to affect the results much less than is done by the unavoidable experimental errors, the mean weight of 1 c.c. of air could be taken as 0.001187 gram. Under these circumstances, the loss of weight in air of the substances weighed is as follows:—

CeO_2 (sp. gr. = 6.7) = 0.000172 gram.

$\text{Ce}_2(\text{SO}_4)_3$ (sp. gr. = 3.9) = 0.000303 gram.

In order to obtain pure cerium preparations, I proceeded as follows:—From 2600 grams of cerite, 1380 grams of crude oxides were obtained by the method described in a former paper. After dissolving the oxides in moderately concentrated nitric acid and removing the excess of acid by evaporation, the remaining *syrup* was dissolved in a little water. On pouring this into a large quantity of *pure* boiling water, almost the whole of the cerium present (about half of the weight of the crude oxides) was precipitated as basic ceric nitrate. This could be easily and quickly washed on a Bunsen funnel with boiling water containing a little nitric acid. I shall call this first precipitate N.

For further purification, instead of using sulphuric acid, as is generally done, nitric acid was employed. This has the great advantage over the old method, that the excess of acid can be very easily removed by evaporation from the solution. If the solution of the resulting ceric nitrate, which is now *crystalline*, be again poured into boiling water, the filtrate will contain, besides the impurities which we wish to remove, *much less* cerium in solution than when sulphuric acid is used. This almost neutral ceric nitrate dissolves easily in a *very large* quantity of water, without undergoing decomposition.

This method, especially the removal of the excess of acid by evaporation, enabled me to carry the purification much further than Wolf was able to do. In using nitric acid, the quantity of cerium is diminished far less rapidly by each precipitation than is the case with sulphuric acid. Whilst Wolf could repeat the process of precipitation only five times, I could obtain, by repeating this tedious process with

A part of the first precipitate only, the following series of precipitates (N) and corresponding filtrates (F), the last being kept separate :—

N	N ₁	N ₂	N ₃	N ₄	N ₅	N ₆	N ₇	N ₈	N ₉	N ₁₀	N ₁₁
F	F ₁	F ₂	F ₃	F ₄	F ₅	F ₆	F ₇	F ₈	F ₉	F ₁₀	F ₁₁ .

Now the question arose which cerium compounds were to be used for the atomic weight determination. After long deliberation, I chose the anhydrous cerous sulphate, as—with the exception of cerous chloride, which H. Robinson had succeeded in preparing only after my experiments were in progress—cerium does not form any other compound of definite composition suitable for the purpose. Bührig rejected cerous sulphate—firstly, because the salt retains free sulphuric acid from the mother-liquor so energetically that it cannot be freed from it even by repeated crystallisations; secondly, because he could not obtain the anhydrous sulphate, the salt retaining traces of water at a moderate heat, and undergoing partial decomposition when heated to incipient redness; and thirdly, he remarks, that on precipitating the solution of the sulphate with barium chloride and afterwards with oxalic acid, the barium sulphate thrown down contains cerium; whilst the cerium oxalate, on the other hand, contains barium, but he does not consider that, if the analysis is to be made by precipitation at all, the process may be executed in the inverse order, without fear of committing the above errors.

The first source of error was avoided in the following way:—Cerous sulphate, prepared by dissolving basic ceric nitrate in dilute sulphuric acid and sulphurous acid, and evaporating the solution in a platinum basin, was heated for some time in a magnesia bath, in order to expel the greater part of the excess of sulphuric acid. The product was then dissolved in a small quantity of ice-cold water, the heavy metals (platinum, &c.) precipitated by hydrogen sulphide, and the excess of the latter expelled first by the use of a water-pump, then by means of a current of air. In this way a solution was obtained, from which, on adding three times its volume of absolute alcohol, the whole of the cerium was thrown down in the form of a fine crystalline powder of the salt $\text{Ce}_2(\text{SO}_4)_3 + 8\text{H}_2\text{O}$. After washing the salt with absolute alcohol, dehydrating at a gentle heat, and again precipitating with alcohol, a completely *neutral* cerous sulphate was obtained. Although free from any excess of sulphuric acid, the salt is not pure, even if it be thrown down from most carefully prepared purified alcohol, it retains traces of foreign organic matter, probably betaine, and consequently turns yellow or brownish on subsequently heating. It dissolves in water, also with a peculiar feeble empyreumatic odour. To purify it, the salt must therefore be once more dissolved in cold water, and after filtering, the solution contained in a beaker is plunged

quickly into boiling water, so as to heat it to 100° . If the hot supersaturated solution be now stirred with a glass rod, the salt present is instantly precipitated as a fine crystalline powder of the composition $\text{Ce}_2(\text{SO}_4)_3 + 6\text{H}_2\text{O}$. This is collected with the aid of the pump on a platinum cone, and can be at once placed in a bottle, for it dries in a few instants when put on a smooth filter-paper.

Originally I had intended to convert the hydrated sulphate by strong calcination into ceric oxide, and to calculate the atomic weight from the relation of the oxide to the hydrated salt, a method which has been used by Nilson and Pettersson (*Ber.*, 13, 1441 and 1453) in determining the atomic weights of beryllium and scandium. Unfortunately all cerous sulphates either alter on exposure to the air, or, if they are stable, they seem to include the mother-liquor in small cavities, a property of salts first noticed by Sorby. On heating the neutral solution of the sulphate to $40\text{--}50^{\circ}$, Marignac's (*loc. cit.*) hydrate, $\text{Ce}_2(\text{SO}_4)_3 + 9\text{H}_2\text{O}$, was never obtained, but instead of this, white turbid crystals of the salt with $8\text{H}_2\text{O}$ always separated out. By spontaneous evaporation in the air at the ordinary temperature, the same salt was obtained in beautiful clear and glistening crystals instead of the salt $\text{Ce}_2(\text{SO}_4)_3 + 12\text{H}_2\text{O}$. At 100° , the salt with $6\text{H}_2\text{O}$ alone is separated, but it quickly alters in the air. It is possible that the hydrates with $5\text{H}_2\text{O}$, $9\text{H}_2\text{O}$, and $12\text{H}_2\text{O}$, which I could not obtain from neutral solutions, crystallise only when free sulphuric acid is present.

For these reasons, I was unable to prepare a cerous sulphate with a definite (theoretical) amount of water of crystallisation which could be used for the atomic weight determination. In only two out of twenty cases in which the water was exactly determined was the theoretical amount of water found, viz., in the clear crystals, $\text{Ce}_2(\text{SO}_4)_3 + 8\text{H}_2\text{O}$, obtained on spontaneous evaporation at the ordinary temperature.

As I had to give up the above plan, I tried to prepare the anhydrous sulphate. It is impossible to obtain it by simply heating the hydrated salt in the air, for at a low temperature the water is not entirely given off, and at about 500° the salt may lose a trace of sulphuric acid, or it absorbs some oxygen and becomes heavier and slightly yellow-coloured by passing partly into ceric salt. But, on following Baubigny's (*Compt. rend.*, 97, 854) example, I found that, at the temperature of boiling sulphur, cerous sulphate entirely loses its water without being decomposed or otherwise altered.

Hitherto it has not been very easy to operate with boiling sulphur, and yet I wanted an arrangement that would allow me to heat the salts for many weeks at 440° without special difficulty. After many trials I succeeded in devising an apparatus for this purpose. A very

thin glass beaker, 18 cm. long and 7 cm. in diameter, is covered with a sheet of thick cardboard, having in its middle a round opening 4 cm. in diameter.* To prevent this cardboard from burning, it is soaked repeatedly with alum, soluble glass, or sodium tungstate. Through the opening in the cardboard is passed a test-tube of thin glass, 20 cm. long and 4 cm. wide, the bottom of the tube being 4 cm. above the bottom of the beaker. The beaker is kept suspended in a wire triangle, and its bottom rests on a piece of thin wire gauze. The beaker is first placed on a sand-bath, and about 50 grams of sulphur are fused in it. Then it is placed on the gauze and heated with 2 or 3 Bunsen's burners, so that the sulphur boils. In this way the whole of the beaker becomes filled with the vapour of boiling sulphur, which condenses on the sides, and flows down again. In order to prevent the upper portion of the beaker from being too strongly heated, the cardboard from carbonising, and the sulphur-vapour from escaping, it is surrounded with a shorter open glass cylinder (a broad beaker with the bottom cut off) about 12 cm. high and 11 cm. wide, covered at the top by a plate of thin sheet copper (15 cm. square), having in its middle an opening of 7 cm., through which the thin long beaker (the sulphur-bath) passes, so that only its lower two-thirds are heated to the boiling point of sulphur, whilst the upper third, being freely exposed to the air, is prevented from becoming too strongly heated. With such an arrangement, the vapour of boiling sulphur reaches to two-thirds of the height of the bath, and the lower part of the test-tube is surrounded by it.

When the cerous sulphate is to be dehydrated, it is placed on a small platinum crucible, and this is suspended by a loop of long thin platinum wire, the upper end of which is bent over the upper edge of the test-tube, in order to prevent the crucible from falling into the boiling sulphur, if the test-tube should crack. (Once, before I made this arrangement, the tube cracked, but, although the crucible was plunged for a quarter of an hour in boiling sulphur, it was not altered in appearance or weight after being washed with potash solution.) The sulphur is then heated slowly to its boiling point, and after a while the platinum crucible is surrounded by sulphur-vapour far above its upper edge. Whilst the greater part of the water of crystallisation of the sulphate is escaping, the test-tube is kept open until a cold beaker held over no longer shows signs of dew. During the operation, the crucible is covered with a lid having the ear cut off, so that there is but very little space between the crucible and the side of the test-tube. When water-vapour ceases to escape, the test-tube is covered with a porcelain crucible lid, and the bath is heated until the weight of the crucible *plus* sulphate is found to be constant. This is easily effected if after one hour's heating the salt be stirred with a

thick platinum wire and heated for another hour. When the operation is finished, the sulphur which has cooled down so that it no longer takes fire in the air, but is still fused, is poured out into a porcelain basin, for if it is allowed to remain in the beaker it would certainly crack either as the sulphur cools or on fusing it again.

When these precautions are observed, the same quantity of sulphur may be kept boiling in this simple apparatus for half a year or longer, from morning to night, without fear of anything happening to it.

When hydrated cerous sulphate is heated in the above apparatus until the weight is constant, and then allowed to cool in a small desiccator containing phosphorus pentoxide, it is found to be perfectly anhydrous, without, however, undergoing the slightest decomposition; the water which escapes from it, and which can be collected on a cool beaker, being neutral and unaffected by barium chloride. If the anhydrous sulphate be heated to a higher temperature in a test-tube, no trace of water is given off, but a mixture of sulphur dioxide and trioxide escapes, so that the decomposition takes place in accordance with the equation $\text{Ce}_2\text{O}_3 \cdot 3\text{SO}_3 = \text{Ce}_2\text{O}_4 + 2\text{SO}_3 + \text{SO}_2$.

This behaviour affords evidence of the powerful reducing power of cerous oxide, and it will be easily understood that it cannot be prepared in the free state. For analysis, the anhydrous sulphate was carefully heated in a double platinum crucible over the flame of an ordinary burner, until sulphur trioxide fumes were no longer given off. In order to expel the last trace of sulphuric anhydride, I tried heating the salt to a white heat in a Fletcher's blast furnace with injector, but I had to relinquish this plan, as not only does the crucible lid become welded to the crucible, but the platinum seems to evaporate perceptibly at this high temperature; the *inner* of the two platinum crucibles which is not exposed to the direct flame, losing in a short time as much as 12 mgrms. If the injector is put in a vertical position, and the air blown in in such a way that the flame, which is generally 30 to 50 cm. long, is converted into a short, hissing, hardly visible one (the flame will be often blown out entirely before the necessary practice is obtained in regulating the air and gas supply), a temperature is obtained *in the free air* at which an ordinary pretty thick platinum wire fuses *instantly*. This is certainly the highest temperature obtainable from a mixture of gas and air without a furnace, and I think that this simple arrangement will prove useful to chemists. The cerous sulphate contained in a double platinum crucible loses every trace of its sulphur at this temperature in 10 to 15 minutes, and it will take weeks before the inner crucible loses 0.0001 gram in weight.

Experiments with Mixtures.

Before the above method of operating with boiling sulphur had been worked out, I tried to decide whether the above precipitate N_4 could be split up into different fractions. For this purpose, one part of it was converted into the neutral sulphate, which was dissolved in water, and then fractionally precipitated with dilute ammonia. I will call the most basic portion remaining in solution A. The precipitate was dissolved in dilute sulphuric acid, and again precipitated. After four precipitations, the least basic portion B was obtained. On heating the hydrated neutral sulphate prepared from the portions A and B high over the flame in a double platinum crucible to constant weight, Wolf's "anhydrous" sulphate (it is really *not* anhydrous) was obtained, and this was converted into ceric oxide by strong calcination. The formulæ used for the atomic weight calculation will be given later on. The following results were obtained :—

Weight of $Ce_2(SO_4)_3$.	Weight of CeO_2 .	Loss of weight.	Per cent. of CeO_2 .	"Atomic weight." $Ce =$
A. { 1·2750 1·3153	0·7717 0·7958	0·5033 0·5195	60·525 60·501	139·83 139·74 } Mean.. 139·78
B. { 1·71305 1·8702	1·03534 1·1308	0·67771 0·7394	60·440 60·404	139·53 139·46 } Mean.. 139·49

These numbers are not absolutely exact, as the water was not entirely expelled, but they may be considered relatively true, for they were determined by the same method. As the "atomic weight" was in one case $Ce = 139·78$, and in the other $Ce = 139·49$, the question remained open whether the material used was homogeneous.

This circumstance suggested an attempt to split up a portion of the precipitate N_3 , which was less pure, but contained only traces of didymium. The basic ceric nitrate from this was converted into cerous sulphate, from which the excess of free acid was removed by alcohol. The aqueous solution of the sulphate was partially precipitated by adding to it strong alcohol, drop by drop, and in this way the portions A, B, C, D were obtained. These precipitated sulphates were dried between smooth blotting-paper, and then in a state of fine powder dehydrated in the sulphur-bath and analysed as before, with the following results :—

Weight of $\text{Ce}_2(\text{SO}_4)_3$.	Weight of CeO_2 .	Loss of weight.	Per cent. of CeO_2 .	"Atomic weight."
A.... 1·3601	0·8241	0·5360	60·591	140·34
B.... 2·4780	1·5009	0·9771	60·568	140·18
C.... 2·3191	1·4041	0·9150	60·545	140·00
D.... 1·5179	0·9245	0·5934	60·906	142·65

The difference in the percentage of ceric oxide of the single fractions is far more striking than in the first case. The oxide obtained from fraction D had a peculiar flesh colour mixed with a pale orange, and it is very remarkable that it turned *grey* under the influence of light, whereas pure ceric oxide is white with a yellowish tint, and does not alter when exposed to light. The portions A, B, and C were far less orange than D. If we assume that the loss of weight on ignition is represented by the same equation as in the case of pure cerous sulphate, viz., $\text{Ce}_2\text{O}_3 \cdot 3\text{SO}_3 - (3\text{SO}_3 - \text{O}) = 2\text{CeO}_2$, the "atomic weight" of the earth metal in the fraction D would be $R = 142\cdot65$.

It will be seen from the numbers given hereafter, that the numbers found for A, B, and C represent very nearly the true atomic weight of cerium. The high percentage of oxide in fraction D cannot be due to the presence of didymium, because anhydrous sulphate of didymium contains only 58·09 per cent. of the oxide, and the peroxide would be completely decomposed at such a high temperature. Still, it might be due to the presence of thorium, its anhydrous sulphate containing 62·42 per cent. of the earth. In order to entirely exclude any thorium possibly present, the following process was used. The earths contained in the filtrates F_1 , F_2 , F_3 , and F_4 were precipitated with potassium hydroxide, and the precipitate, consisting chiefly of cerous hydroxide, was suspended in strong caustic potash solution, and treated for three days with chlorine, in order to remove the greater part of the lanthanum and didymium present. After thoroughly washing, the precipitated ceric hydroxide was dissolved in nitric oxide, and the excess of acid removed by evaporation, when a gelatinous mass of ceric nitrate was obtained. Its solution in cold water was poured into boiling water, and so the greater part of the purer cerium salt was thrown down as basic nitrate. From the filtrate containing impure cerium salt, the earths were thrown down with ammonia and converted into the sulphates. After dissolving in five parts of ice-cold water and separating the heavy metals with hydrogen sulphide, the solution was heated at 60—70° for some time. At this temperature most of the cerous sulphate separates out, and if any thorium be present, its sulphate will, according to Nilson's experiments (*Ber.*, 15, 2519), also crystallise out. The same holds

good as regards lanthanum sulphate. The last mother-liquor contains, besides cerium, some didymium. It was split up into two parts by adding strong alcohol, and the *last* precipitate (*i.e.*, the most soluble salt) was recrystallised from water and used for the atomic weight determination :—

$R_2O_3, 8SO_3$.	RO_2 .	Loss of weight.	Per cent. of RO_2 .
1·8649	1·1459	0·7190	61·444
2·4310	1·5011	0·9299	61·185
0·7863	0·4829	0·3034	61·414
			Mean.... 61·331

This strikingly high percentage of oxide, if calculated out in accordance with the above equation, would correspond with an "atomic weight" of $R^{III-IV} = 145·72$.

The material was not entirely free from didymium, and, although it was improbable, for the reasons stated, that its presence could render the percentage of the oxide higher, experiments were undertaken with cerous sulphate artificially contaminated with a little didymium salt, in order to decide the question. The following negative results were obtained :—

Sulphate.	Oxide.	Per cent. of oxide.
0·6941	0·4203	60·55
1·6320	0·9878	60·53

I could not yet decide the question as to whether the presence of one of the many rare earths, some of which have been but very little studied up to this time, makes the atomic weight of impure cerium higher, neither could I find out the reason of the high numbers obtained. In any case, it is seen from the above experiments, that under certain conditions "cerium" may consist of a *mixture*. The nature of this admixture must be ascertained by further experiments; but before this is done we must become acquainted with the properties of really pure cerium.

Experiments with Pure Material.

The object of the following series of experiments was to ascertain how far cerium has to be purified in order to furnish a truly homogeneous product. For the experiments, the following of the above-mentioned precipitates of basic nitrate and the corresponding filtrates were used :—

N ₅	N ₆	N ₇	N ₈	N ₉	N ₁₀	N ₁₁
F ₅	F ₆	F ₇	F ₈	F ₉	F ₁₀	F ₁₁ .

These were found to be entirely free from lanthanum and didymium.

It will be seen from an inspection of this series, and a consideration of the process of fractionation, that the cerium in the *filtrates* is far more strongly "fractionated" than the *precipitates*, especially as the quantity of earth in each filtrate is much smaller than that in the corresponding precipitate. For this reason the filtrates alone were used to determine the question of homogeneity, and, as no fundamental stoichiometric numbers were to be obtained, the following simple process was used for the preparation of cerous sulphate from them:—The filtrates, after adding to them some of the sulphuric acid, and later on some sulphurous acid, were evaporated to dryness in a platinum basin, and from the sulphates obtained in this way the excess of sulphuric acid was driven off by heating the residue in a magnesia-bath; it was then dissolved in water, and the sulphate thrown down by alcohol. After repeating this process, the anhydrous sulphate was dissolved in water, and the neutral sulphate separated out by heating the solution at 100°. The dehydration in the sulphur-bath and the analysis were carried on in the way described above. The results are given in uncorrected numbers:—

Filtrates.	Ce ₂ (SO ₄) ₃ .	CeO ₂ .	Per cent. of CeO ₂ .
F ₅ {	2·3797 1·8258	1·4424 1·1073	60·614 60·648
F ₆ + F ₇ The two together....	2·2670 2·1869	1·3749 1·3252	60·649 (maximum). 60·597 (minimum).
F ₈ + F ₉ The two together....	2·5807 2·0149	1·5648 1·2216	60·634 60·627
F ₁₀ + F ₁₁ The two together....	1·6519 1·6193	1·0018 0·9815	60·615 60·612
			Mean.... 60·624

The material used for these experiments, although containing no other earth metal but cerium, had been too much in contact with filter-paper, with glass and porcelain vessels in strongly acid solution, and with air, so that the numbers were neither corrected, nor were they used for the calculations of the atomic weight. But, as they are for all fractions exactly the same, showing neither a regular increase nor decrease, and differ from the mean number at the outside by $\pm 0\cdot025$ of a unit in percentage, the conclusion must be drawn

that the cerium of the filtrates F_8 to F_{11} is a *perfectly homogeneous body*.

Now it remained only to use the last of all the precipitates, viz., N_{11} , containing the best purified cerium, for the *definite* atomic weight determination, and to ascertain whether, on comparing it with the filtrates mentioned above, it furnishes the same results. For the same purpose, in I and II (see table), part of the precipitate N_{10} was used. The remaining 21 determinations were made with a material obtained from *different preparations*, in order to meet the objection that only one kind of material had been used. For, in such a case, even if the results agreed, they might not be accurate. It is almost unnecessary to remark that the following series of determinations was made with the greatest possible care, and that they involve the correction both of weights and for displaced air. I did not exclude one single experiment which I made, not even numbers XIV and XXIII, although they may be considered a little too low, for the difference of weight to which these low numbers are due, falls within the allowed experimental errors.

Number of experiment.	Cerous sulphate.	Ceric oxide.	Loss by calcination.	Percentage of CeO_2 .	Atomic weight of cerium.
I..	2·16769	1·31296	0·85473	60·5695	140·183
II..	2·43030	1·47205	0·95825	60·5707	140·191
III..	2·07820	1·25860	0·81960	60·5620	140·128
IV..	2·21206	1·33989	0·87217	60·5721	140·201
V..	1·28448	0·77845	0·50603	60·6043	140·433 (max.)
VI..	1·95540	1·18436	0·77104	60·5687	140·176
VII..	2·46486	1·49290	0·97196	60·5673	140·167
VIII..	2·04181	1·23733	0·80448	60·5997	140·400
IX..	2·17714	1·31878	0·85836	60·5739	140·215
X..	2·09138	1·26654	0·82494	60·5600	140·114
XI..	2·21401	1·34139	0·87262	60·5863	140·304
XII..	2·44947	1·48367	0·96580	60·5711	140·194
XIII..	2·22977	1·35073	0·87904	60·5771	140·237
XIV..	2·73662	1·65699	1·07963	60·5488	140·033 (min.)
XV..	2·62614	1·59050	1·03564	60·5642	140·144
XVI..	1·67544	1·01470	0·66074	60·5632	140·137
XVII..	1·57655	0·95540	0·62115	60·6007	140·407
XVIII..	2·72882	1·65256	1·07626	60·5600	140·110
XIX..	2·10455	1·27476	0·82979	60·5716	140·198
XX..	2·10735	1·27698	0·83037	60·5965	140·377
XXI..	2·43557	1·47517	0·96040	60·5678	140·170
XXII..	3·01369	1·82524	1·18845	60·5649	140·150
XXIII..	4·97694	3·01372	1·96322	60·5537	140·068
Total....	53·77424	32·57367	21·20057	60·5747	140·2210

For the calculation of the atomic weight Lothar Meyer's and Seubert's example was followed, viz., the several amounts of sub-

stance weighed were added together, and the atomic weight calculated from the totals according to the following formula. (It has been proved mathematically by Ostwald, that such a method of calculation is correct.)

$$\text{Ce}_2(\text{SO}_4)_3 : 2\text{CeO}_2 = 53.77424 : 32.57367 \text{ grams,}$$

when if $\text{Ce}_2(\text{SO}_4)_3 = 100$, $\text{CeO}_2 = 60.5747$.

Difference of $\text{Ce}_2(\text{SO}_4)_3$ and CeO_2 (loss of weight) = 21.20057 grams.

$$\frac{32.57367 \times (3\text{SO}_3 - \text{O})}{21.20057} = 2\text{CeO}_2, \quad \frac{2\text{CeO}_2 - 4\text{O}}{2} = \text{Ce.}$$

If we replace all by numbers and take for O = 16 and S = 32.06, we have $(3\text{SO}_3 - \text{O}) = 224.18$; then we have—

$$\begin{array}{r} \frac{32.57367 \times 224.18}{21.20057} = \frac{344.4420}{64} \\ \frac{2\text{Ce} = 280.4420}{\text{Ce} = 140.2210.} \end{array}$$

If calculated with hydrogen numbers, O = 15.96 and S = 31.98, then—

$$\text{Ce} = 139.8707.$$

I have *not* calculated the atomic weight and its probable error by the method of least squares, because the following different numbers have been calculated by different chemists (for O = 16) as the atomic weight of sulphur on which such a calculation should be founded.

Stas	32.074
Ostwald	32.0626
Sebelien*	32.0608
L. Meyer and Seubert	32.0592
Clarke.....	32.058

The extreme difference of these numbers is = 0.016, and the calculation of the probable error would become uncertain.

It is, no doubt, a very good principle to determine the atomic weight of an element by several independent methods; unfortunately it was impossible in the above case from want of choice of suitable cerium compounds. I have tried to obviate this objection by making a greater number of determinations.

On the other hand, my number is severely controlled by the numbers

* Sebelien, *Beiträge zur Geschichte der Atomgewichte*, Braunschweig, 1884, p. 155.

found by Robinson (*loc. cit.*) for both numbers, determined by widely different methods, are in as good an accordance as can be expected:—

	Robinson.	Brauner.
For O = 16 Ce =	140·2593	140·2210
For O = 15·96 Ce =	139·9035	139·8707.

If we compare the above series of determinations with that made for the purpose of investigating the homogeneous nature of cerium (from the filtrates F_8 to F_{11}), both series are seen to agree well, and from this the conclusion must be drawn that the pure cerium preparations used by me were *homogeneous*.

The simple method which I adopted for the purification of cerium preparations must be considered very good, as from 1380 grams of crude oxides, containing in all 690 grams of ceric oxide, I obtained 720 grams of *pure* nitrate, representing over 500 grams of ceric oxide.

Discussion of Former Determinations of the Atomic Weight of Cerium.

It will be almost unnecessary to discuss several of the above quoted determinations, for they were carried out with a material containing other cerite metals. This may be said of the experiments made by Hisinger in 1814–16, by Beringer in 1842, and by Rammelsberg in the same year. The method followed by Hermann (1843) and by Marignac (1848), viz., precipitation of the sulphuric acid in a solution of cerous sulphate with barium chloride, has been declared by Marignac himself to involve a considerable source of error, as the barium sulphate carries down some cerium with it. Besides, for the reasons given by Bührig, and quoted above, it is very improbable that the sulphate used by these and other authors (especially by Jögel) had a definite *normal* composition.

Jögel (in 1858) and Rammelsberg (in 1859) determined the atomic weight of cerium by the combustion of cerous oxalate. It has been shown by Nilson (*Ber.*, 15, 2519) in his paper on the atomic weight of thorium, that the method of elementary analysis of an oxalate involves several errors which make it unsuitable for the exact determination of the atomic weight of an element.

I shall therefore not enter more fully into an analysis of the papers published up to 1860, but proceed to discuss the work done by Wolf. As regards, first of all, his observation that the atomic weight of cerium *diminishes* on further purification of the preparations, I think it may be regarded as *confirmed* by my own experiments. But this decrease ceases as soon as we get to the precipitate N_8 (it would correspond to Wolf's N_6 which, however, he never obtained). Wolf's ceric oxide was *white*. The same was the case with my *purest* ceric oxide, though I should prefer to call it the palest "*chamois*."

On the other hand, I cannot confirm the very low atomic weight found by Wolf. Firstly, Wolf did not prove that his sulphate had a definite normal composition. His hydrated salt, as can be concluded from my own experiments on this subject, most probably did not contain the theoretical amount of water of crystallisation, and according to Bührig it must have contained some free sulphuric acid, which can be got rid of only by the process quoted above. If these two sources of error are not taken into consideration, the atomic weight of cerium will be found *lower* than it really is. As regards the numbers calculated from the "anhydrous" sulphate, they cannot be regarded as exact, for cerous sulphate, heated high over a small flame in a double platinum crucible, retains a trace of water, as has been already pointed out by Bührig, and as may be seen from the following experiment.

3.0283 grams of crystallised cerous sulphate gave, on heating for two hours in a double platinum crucible at a temperature at which the bottom of the outer crucible was red hot for a short time (the temperature applied by Wolf was never so high), 2.3843 grams of "anhydrous" salt. On heating it in the sulphur-bath at 440° , it lost the last trace of its water, and its weight diminished by 0.0046 gram, namely to 2.3797 grams. As at a high temperature the sulphate yielded 1.4424 gram of CeO_2 , the atomic weight, calculated from the first number, would be $\text{Ce} = 139.65$ instead of $\text{Ce} = 140.22$.

Secondly, I found that, on precipitating a solution of cerous sulphate with boiling oxalic acid solution, a trace of cerium, the oxalate of which is partly soluble in the free sulphuric and oxalic acids, remains in solution even after long standing.

1.3506 gram of anhydrous sulphate, precipitated and ignited by Wolf's method, gave 0.8173 gram $\text{CeO}_2 = 60.514$ per cent. Directly analysed, the same sulphate gave 60.60 per cent. of CeO_2 . This error, although slight, gives a smaller atomic weight.

Thirdly, on precipitating the filtrate from the cerous oxalate with barium chloride, a little more barium sulphate is always obtained than corresponds with the sulphuric acid contained in it, for not only is the trace of cerium which remains in solution carried down with barium sulphate, but also some barium oxalate. This causes the atomic weight of cerium found to be lower.

From the above filtrate, after separation of cerous oxalate, 1.6831 gram of BaSO_4 , corresponding with 0.5781 gram, or 42.803 per cent. of SO_3 , was obtained (theory requires only 42.24 per cent). From the relation of 0.8173 CeO_2 : 0.5781 SO_3 , the atomic weight calculated is $\text{Ce} = 137.78$ instead of $\text{Ce} = 140.22$.

If only one or all of these sources of error are left out of consideration, the atomic weight of cerium found will always be lower than the

true one. I think, therefore, that I have sufficiently explained the low numbers found by Wolf.

In striking contrast with Wolf's work is that done by Bührig, who found the high number $Ce = 141.5$. Bührig analysed large quantities of cerous oxalate by combustion (the details will be found in Clarke's recalculation), but he made the mistake of using a material resulting from one preparation only. I do not believe, however, that Bührig's oxalate contained an admixture of basic salt, as is sometimes stated.

Another cause of error in Bührig's work must be looked for in the fact, as Nilson has shown (*loc. cit.*), that the analysis of oxalates by combustion is subject to constant errors which make the atomic weight *higher*. For example, Cleve, by this method, found the atomic weight of thorium to be $Th = 233.80$ to 233.97 , whereas Nilson's analysis of the sulphate gave $Th = 232.40$.

But, as Bührig used for combustion large quantities of oxalate—about 10 grams at once—the loss of carbonic anhydride and the *plus* of water cannot have been the only source of the difference between the number obtained and the true one. I am inclined to believe that the reason of Bührig's higher number was partly the same which caused me to find the "atomic weight" of the *impure* cerium to be $R = 142.65$, and even $R = 145.72$, for Bührig points out distinctly that his oxide was yellow. Further, as this oxide when strongly heated is converted with loss of weight into one which is of a pale salmon colour, the former may have contained some of the unstable peroxide, the admixture of which would cause the atomic weight found to be a little higher.

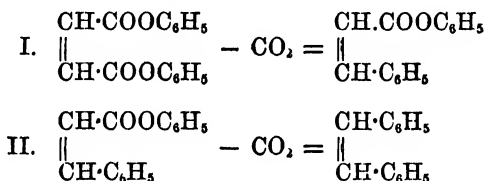
In conclusion, it may be pointed out that, in consequence of the present new determinations, the differences between the atomic weights of lanthanum, cerium, and didymium, elements following each other in the periodic system, harmonise far more than was previously the case. Thus we have,

La.	Ce.	Di.
138.2	140.2	142.3
Difference... 2.0		2.1

LXXXI.—A New Method of Preparing Aromatic Hydrocarbons.

By RICHARD ANSCHÜTZ.

IN the course of a research on fumaric acid and maleïc acid, Wirtz and I noticed that a hydrocarbon was formed when phenylic fumarate was distilled. This hydrocarbon was found to be stilbene, and its formation may be accounted for on the supposition that the phenylic fumarate loses 2 mols. of carbon dioxide. Phenylic cinnamate must be considered to be the first product of the reaction, and this in its turn gives off carbon dioxide, becoming stilbene, as represented by the following equations:—



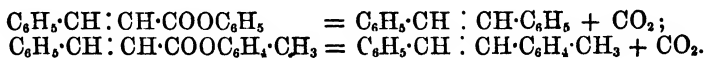
Led by this consideration, I submitted several aromatic cinnamic ethereal salts, prepared by Mr. Selden at my suggestion, to slow distillation under ordinary pressure. In each case, I noticed that there was an evolution of carbon dioxide during the distillation, and that afterwards products of decomposition distilled over.

All the cinnamic ethereal salts were prepared by heating the phenol with pure cinnamic chloride (b. p. 140° under about 16 mm.).

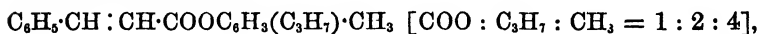
Phenylic cinnamate, $\text{C}_6\text{H}_5 \cdot \text{CH} : \text{CH} \cdot \text{COOC}_6\text{H}_5$, melts at 72·5°; it is readily soluble in alcohol, and boils under a pressure of 15 mm. at 205—207° without decomposition. The hydrocarbon obtained from it by slow distillation under ordinary pressure proved to be stilbene: it fused at 124°, and when treated with bromine gave stilbene bromide, sparingly soluble in alcohol and chloroform, and melting at 235°.

Paracresylic cinnamate, $\text{C}_6\text{H}_5 \cdot \text{CH} : \text{CH} \cdot \text{COOC}_6\text{H}_4 \cdot \text{CH}_3$ [COO : CH_3 = 1 : 4], melts at 100—101°; it is more sparingly soluble in alcohol than the phenylic salt, and under 15 mm. pressure boils at 230° without decomposition. On slow distillation under ordinary pressure, it yields methylstilbene, a substance very similar to stilbene; this crystallises from alcohol in plates which melt at 120°, and exhibit a beautiful blue fluorescence. When treated with bromine in a solution of chloroform, methylstilbene gives a bromide readily soluble in chloroform, but only very sparingly soluble even in boiling alcohol; after being recrystallised from alcohol, it melts to a brown liquid.

The decomposition of the two ethereal salts in question on slow distillation, under ordinary pressure chiefly takes place, therefore, in accordance with the equations—



Thymylic cinnamate,



melts at 69—70°, and under about 15 mm. pressure distils at 239—240° without decomposition. On heating it under ordinary pressure, carbon dioxide is given off, but the liquid substances obtained from it have not yet been studied.

β-Naphthyl cinnamate, $\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{COOC}_{10}\text{H}_7$, melts at 101—102°, and gives, on distillation under ordinary pressure, a large quantity of hydrocarbon, sparingly soluble in alcohol; when recrystallised from alcohol, this forms glistening plates which melt at 145°, and are readily soluble in chloroform. The bromide is readily soluble in chloroform, and can be recrystallised from boiling alcohol, in which it is very sparingly soluble; it melts at 192°, becoming black.

Phenyl succinate which, according to Weselsky, boils undecomposed at 320°, may be completely decomposed by slow heating, carbon dioxide being evolved. Amongst the products of decomposition, *di-benzyl* is only found in very small quantity; lower boiling substances smelling of phenol are chiefly produced, but these have not yet been studied. As it is evident that the reaction described may be generalised, the study of the conditions under which carbon dioxide is split off from ethereal salts of carboxylic acids has been commenced in the Bonn Laboratory.

LXXXII.—On the Decomposition of Aromatic Ethereal Salts of Fumaric Acid.

By RICHARD ANSCHÜTZ and QUIRIN WIRTZ.

WE have for some time been occupied with the study of the action of phosphorus pentachloride on maleic anhydride. W. H. Perkin (*Ber.*, 14, 2548), who has examined this reaction, states that on distilling maleic anhydride with phosphorus pentachloride, as might have been expected, fumaric chloride is produced. The reaction, however, is not a complete one, and a great part of the unaltered anhydride passes over towards the end of the operation. We have

worked in such a manner that after the reaction was completed, we distilled the products under diminished pressure, and after repeated fractional distillation, we succeeded in isolating a liquid boiling at 70—71° under about 11 mm. pressure; this on analysis gave numbers which are in accordance with the formula of maleïc chloride. We observed that fumaric chloride boils under 14 mm. pressure at 60°.

Circumstances compelled us to discontinue the experiments for three months, and during this time the product of the action of phosphorus pentachloride on maleïc acid anhydride remained untouched, sealed in a glass tube. On continuing the research we subjected the liquid which previously boiled at 70—71° under 14 mm. pressure again to rectification under diminished pressure. The chloride now began to boil at 60° under 14 mm. pressure, the temperature rising to 75° towards the conclusion of the distillation, so that the chloride had evidently changed its nature.

As one of us had formerly (*Ber.*, 12, 2281) observed that maleïc acid is completely changed by acetyl chloride into its anhydride, and that maleïc acid is not converted to fumaric acid by dry hydrogen chloride, it seemed possible that two different ethereal salts would be produced if fumaric chloride and the product of the reaction of phosphorus pentachloride on maleïc acid were treated with a dry alcohol.

By the hydrolysis of the ethereal salts prepared from the product of the reaction of phosphorus pentachloride on maleïc acid anhydride we might obtain the desired information as to the nature of the chloride produced. This consideration induced us, in the first place, to prepare phenylic fumarate from fumaric chloride and phenol, because—of the more easily obtainable alcohols—phenol is the most readily secured free from water.

$\text{CH}\cdot\text{COOC}_6\text{H}_5$
Phenylic fumarate, \parallel , crystallises from alcohol in white
 $\text{CH}\cdot\text{COOC}_6\text{H}_5$

needles melting at 161—162°, very sparingly soluble even in hot alcohol. If rapidly distilled, it passes over partly unchanged, but is partly decomposed into carbon dioxide and *stilbene*. If phenylic fumarate is heated very slowly, it is almost wholly decomposed in this manner, an oil of aromatic odour, which we have not yet studied, accompanying the *stilbene*.

The explanation of this reaction, which is given in the preceding communication, involves the intermediate formation of phenylic cinnamate; the correctness of our explanation would be placed beyond doubt if we could succeed in finding this compound among the products of the decomposition. We therefore tried to conduct the reaction step by step, and ceased heating the phenylic fumarate as

soon as half the quantity of carbon dioxide formerly observed had been expelled. The residue in the fractionating flask was distilled under diminished pressure, and the solid distillate recrystallised from alcohol. The greater part of it consisted of stilbene, but we succeeded without difficulty in isolating *phenylic cinnamate* from the alcoholic mother-liquor; this on treatment with an alcoholic solution of potash, gave pure cinnamic acid.

Paracresylic fumarate, $\begin{array}{c} \text{CH}\cdot\text{COOC}_6\text{H}_5 \\ \parallel \\ \text{CH}\cdot\text{COOC}_6\text{H}_5 \end{array}$, is very sparingly soluble in alcohol, and melts at 162° ; it is decomposed when heated, losing carbon dioxide and yielding two crystalline substances, one of which is sparingly, the other easily soluble in alcohol. The former is *dimethylstilbene* melting at 179° . It gives a bromide, easily soluble in chloroform and very sparingly soluble in alcohol, melting with decomposition at $203\text{--}204^\circ$. The soluble substance melts at 79° and crystallises in glistening scales; it is perhaps phenylic methylcinnamate.

From these results it follows that hydrocarbons belonging to the stilbene group may be prepared from the fumaric and cinnamic acid ethers of the monohydric phenols, and of course the ethers of cinnamic acid, with the exception of the phenyl ether, give hydrocarbons with different aromatic radicles—that is, “mixed stilbenes;” whilst the fumaric acid ethers give hydrocarbons with the same aromatic radicles, that is, “symmetric stilbenes.” Moreover, the fumaric ethers of the phenols give phenyl ethers of acids belonging to the cinnamic acid group.

The formation of stilbene from phenyl fumarate is of special interest also, from the hydrobenzoins being brought into near relation with fumaric acid by this transition, although in an indirect manner. We shall endeavour to prepare the acetyl ethers of the hydrobenzoins from the phenyl ethers of the acetyltartaric acids by elimination of carbon dioxide.

LXXXIII.—*The Influence of Silicon on the Properties of Cast Iron.*
Part II.

By THOMAS TURNER, Assoc. R.S.M. (Demonstrator of Chemistry,
Mason College, Birmingham).

THE present paper is a continuation of one recently published (this vol., p. 577) in which an account was given of a series of experiments intended to determine the influence of the regulated and gradual addition of silicon to cast iron of more than usual purity. A description has already been given of the general method of procedure, the composition of the materials used, and the analyses of the metal obtained. Experiments were also described by which the influence upon tensile strength and modulus of elasticity was gradually made clear, and the effect upon the proportion of graphitic carbon shown. A further account, though necessarily incomplete, was also given of the appearance on fracture, the relative fluidity of the melted material, the appearance of the castings, soundness of metal, and resistance to fracture. Other experiments have now to be mentioned in connection with the influence of silicon on the physical and mechanical properties of cast iron.

Specific Gravity.—The specific gravity of the specimens might obviously be determined in two ways: on the one hand by the employment of fragments such as borings or turnings, or on the other by the use of pieces of considerable size. It appeared at first doubtful which of these two methods was to be preferred. It had been already shown that the 10 specimens to be operated upon varied very much in tenacity and hardness, and it therefore appeared probable that their density would be unequally affected by the different forces exerted upon them while being reduced to small fragments. On the other hand, the presence of any unsoundness in the specimen would have a much greater influence upon the result if large masses were employed. Under these circumstances, it was considered best to determine the specific gravity both in a turned piece of considerable size, and in the turnings from the specimen.

For the determination of the specific gravity in mass, it was considered best to employ large pieces all as nearly as possible of one size. For this purpose, cylinders 3 inches long and 1 inch in diameter were prepared, each weighing upwards of 270 grams, whilst their maximum difference of water displacement did not vary more than ± 0.06 gram, except in one instance, where the specimen afterwards proved to be unsound. The pieces were washed with alcohol to free

them from any accidental grease, and suspended by a fine platinum wire in water at 20°.

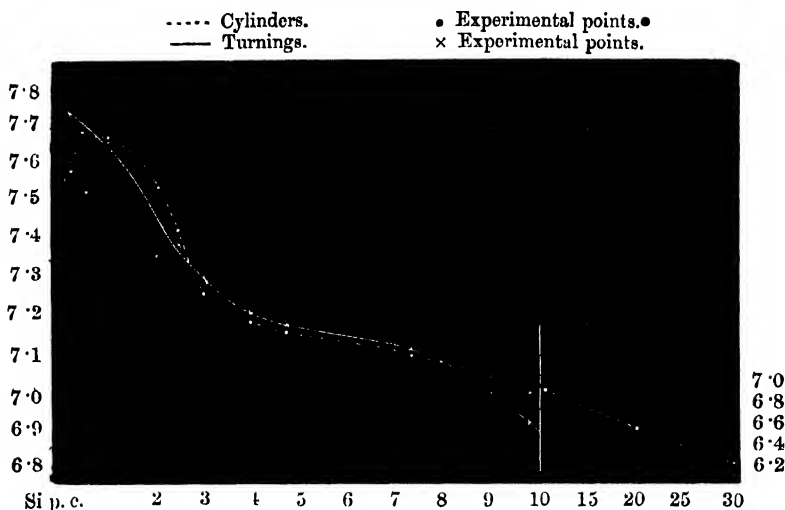
The turnings produced during the preparation of the cylinders were used for the determination of the specific gravity of fragments. To avoid any mistake, the specimens were served out singly to the workman, and the operation personally superintended throughout, each cylinder being marked, and the turnings labelled, before another specimen was commenced. In the determination itself, a modified Sprengel tube (Nicol, *Phil. Mag.*, June, 1885, 455) was employed, by which considerable weights of metal could be operated upon, 17·5 grams being the least quantity employed. The tubes were filled with paraffin oil, of sp. gr. 0·79215, and immersed in a Nicol's (*Phil. Mag.*, May, 1883, 339) constant temperature bath. In each case where much difference existed between the specific gravity of the cylinder and that of the turnings, duplicate experiments were made, and as these always agreed well together, it is probable that very tolerable accuracy was obtained. The results are given in the following table:—

TABLE C.—*Specific Gravity of Cast Iron at 20° C.*
(Water at 20° = 1.)

Silicon per cent.	Sp. gr. of cylinders.	Sp. gr. of turnings.
0·19	7·560	7·719
0·45	7·510	7·670
0·96	7·641	7·630
1·96	7·518	7·350
2·51	7·422	7·388
2·96	7·258	7·279
3·92	7·183	7·218
4·75	7·167	7·170
7·37	7·128	7·138
9·80	6·978	6·924

It will be noticed that there is not generally a very marked difference between the values obtained by the different methods. The turnings from the three strongest specimens, however, show a *diminished* density (compare this vol., p. 580), and this is particularly marked in the middle one of the three, containing 1·96 per cent. Si, which possesses the highest tenacity of the series. On the other hand, the rest of the turnings, with the exception of silicon pig itself, show an *increased* density due to the mechanical force exerted during turning. In the case of the cylinder containing 0·45 per cent. Si, the specimen was afterwards proved to be faulty in the interior, and this evidently accounts for its irregularity.

FIG. 3.—SPECIFIC GRAVITY.



In Fig. 3 these facts are expressed graphically, the curve being continued, on a reduced scale, with data obtained from *Watts' Dictionary*, 1st Suppl., p. 753, where an account is given of some silicides of iron prepared by Hahn.

Relative Hardness.—The smooth ends of the cylinders employed in specific gravity experiments were used for the determination of relative hardness. It had been originally intended to do this by means of a weighted steel point, but, on the advice of Dr. Nicol, a cutting diamond was substituted for the steel point. The diamond was firmly fixed, vertically, point downwards, into the end of a long lath, and at right angles to its length. The lath was then balanced in the middle, and fixed so as to allow of free motion in a horizontal plane. The smooth end of the cylinder to be operated upon was brought underneath the diamond, and weights added until a perceptible scratch was produced on drawing the diamond across the surface of the metal. A note was made of the weight which had been added, and this was gradually diminished until no visible scratch was produced on again drawing the diamond over the metallic surface. The difference between the two observations was generally 5 grams, and, on repeating the observation upon the same specimen, the results obtained did not vary from each other by more than the same amount. In observations of this kind, it was not considered necessary to use weights smaller than a gram.

The mean of the two observations was taken, as the point desired,

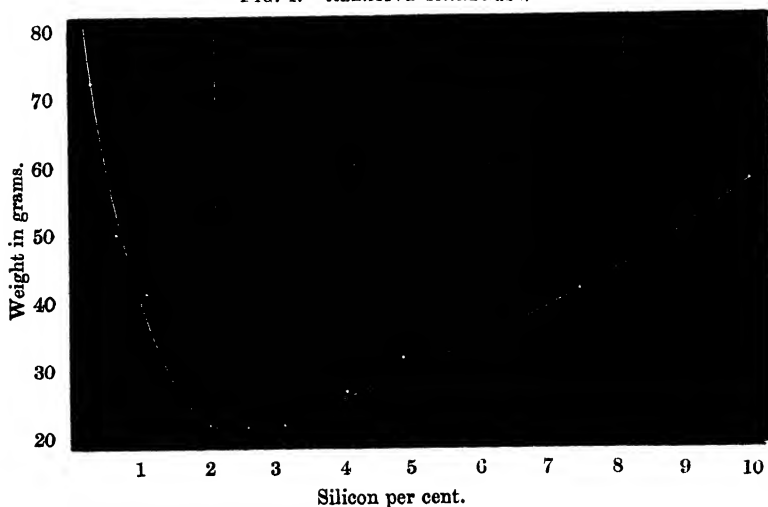
and the results obtained are given in Table D (below). It will be noticed that pure cast iron is the hardest of the whole series, and that the hardness is diminished by the addition of silicon up to 2 per cent. There is then no appreciable difference until 3 per cent. has been added, after which the metal is gradually rendered harder by continued addition of silicon.

TABLE D.—*Relative Hardness.*

Silicon per cent.	Weight in grams.
0.19	72
0.45	52
0.96	42
1.96	22
2.51	22
2.96	22
3.92	27
4.75	32
7.37	42
9.80	57

These results may be graphically represented in a curve, as we have in Fig. 4, when it will be seen that the change produced is gradual and quite regular.

FIG. 4.—RELATIVE HARDNESS.



Working Qualities.—During the preparation of the cylinders pre-

viously mentioned, especial notice was taken of the working qualities of the iron. The observations were made by an experienced workman, and they agree very nearly with the determinations of hardness given above.

0 per cent. Si. Very hard indeed; rather unsound under the skin, but turned bright.

0.5 per cent. Si. Very hard, though not so hard as the previous specimen; there were several blowholes under the skin, and the specimen proved unsound when tested afterwards.

1 per cent. Si. Hard, though softer than the last specimen; cut well, gave bright surface, and was quite sound.

2 per cent. Si. Good, sound, ordinary, soft cutting iron, of excellent quality; turned surface darker in colour.

2.5 per cent. Si. Rather harder than the last, but otherwise the same.

3 per cent. Si. Like 2 per cent.

4 per cent. Si. Like the latter, but rather harder.

5 per cent. Si. Cuts rather harder than 4 per cent., though not unusually hard.

7.5 per cent. Si. Still harder, and cuts very like the next specimen. The turned surface is not so smooth.

10 per cent. Si. Hard cutting iron, though still much softer than the first specimen (0 per cent.).

The appearance of the turnings is also characteristic. These, at either end of the series, are small and of irregular shape, gradually passing into the longer curly turnings of good cutting iron as they approach the 2—3 per cent. specimens.

Crushing Strength.—For the determination of the crushing strength, it was originally intended to employ the cylinders 3 inches long by 1 inch diameter, which had been used in the specific gravity experiments. But as the specimens were of unusual strength, it was found necessary to reduce the diameter to 0.75 inch. The specimens were tested by Professor A. B. W. Kennedy, at University College, and I have again to express my obligation to him for the kindly interest he has manifested in these experiments. The results obtained are given in Table E (p. 907). The exact composition of each specimen has already been given (this vol., p. 581).

TABLE E.—*Crushing Strength.* (Tests by Professor Kennedy.)

Silicon per cent.	Breaking load per square inch.	
	Pounds.	Tons.
0	168,700	75.30
0.5	204,800	91.42
1	207,300	92.54
2	135,600	60.53
	139,000	62.05
2.5	172,900	77.18
3	128,700	57.45
4	106,900	47.74
5	103,400	46.16
7.5	111,000	49.55
10	76,380	34.10

These figures illustrate the same fact, before shown in several ways, that on addition of small quantities of silicon the metal improves in quality, but gradually becomes inferior on the addition of larger percentages. This is shown graphically by the curve given in Fig. 5 (p. 908), and for comparison the curves of tensile strength and modulus of elasticity have been drawn to suitable scales, and are given in the same diagram. All three curves show the same general characters, though it will be noticed that the maximum point is different in each case; this difference, however, is not very considerable.

It will be observed that only six of the experimental results, or two-thirds of the whole, agree well with the curve drawn. But it must be remembered that this class of mechanical tests is more liable to variation than most others, errors of ± 5 per cent. not being uncommon in different specimens of the same material; and, as two of the results are high, and the other two low, there can be little doubt as to the general shape of the curve. This curve must, therefore, be regarded more as indicating a general tendency than as a rigid representation of fact.

In Fig. 6 (p. 909 *et seq.*) we have full-sized sketches of the test pieces after fracture. They are of interest as showing that greatest plasticity is produced by the addition of a moderate amount of silicon, say about 2—3 per cent.

The following remarks were made by Professor Kennedy on the character of the test pieces:—

0 per cent. Surface smooth and silvery along planes of shear, very fine grained, and light in colour where fairly fractured.

* This result, being somewhat irregular, was repeated.

FIG 5.—EFFECT OF SILICON ON CAST IRON—CRUSHING STRENGTH.

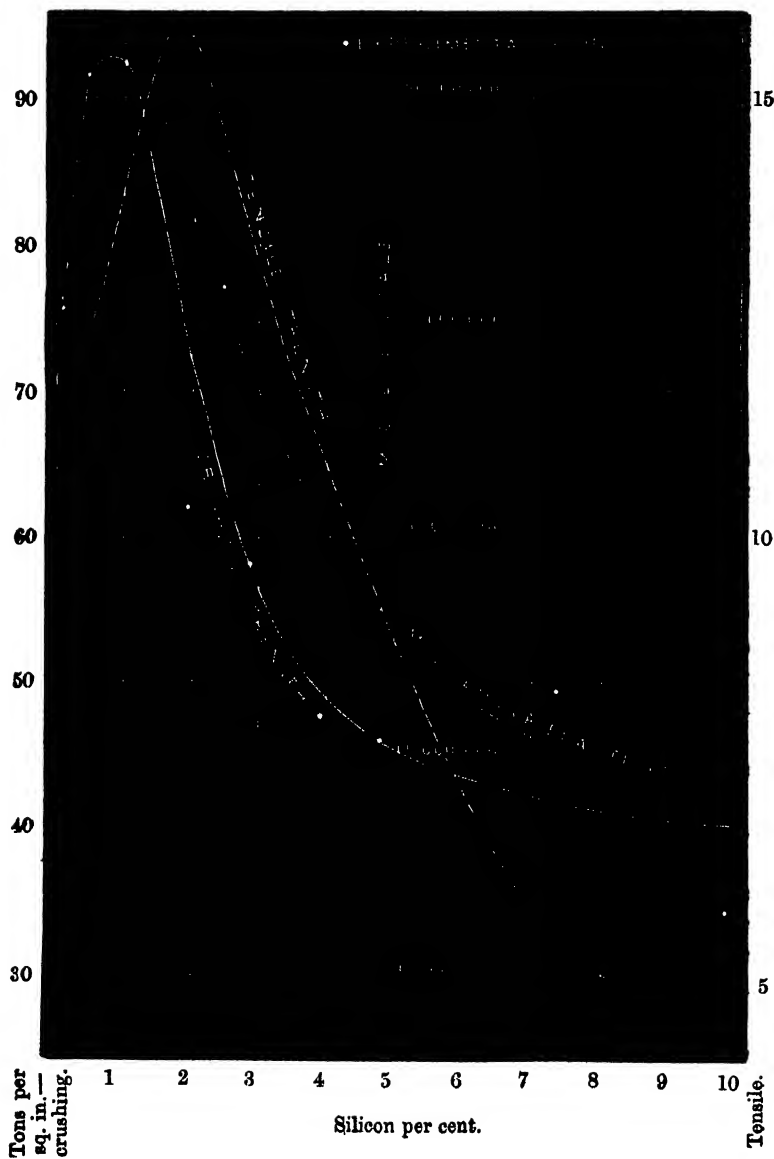


FIG. 6.—FULL-SIZE SKETCHES SHOWING FRACTURES (Professor Kennedy).



0 per cent. Si



0.5 per cent. Si.



1 per cent. Si.



2 per cent. Si.



2 per cent. Si.



2.5 per cent. Si.



3 per cent. Si.



4 per cent. Si.



5 per cent. Si.



7.5 per cent. Si.



10 per cent. Si.

0·5 per cent. In greatest part silvery, but at A close grained grey crystals.

1 per cent. Very irregular, in part split longitudinally, part transversely, showing planes smooth and silvery. Direct fracture as in sketch.

2 per cent. Silvery grey ; at AA close grained grey crystals.

2·5 per cent. Very slightly distressed on surface.

3 per cent. Surface silvery along shearing planes.

4 per cent. Do. do.

5 per cent. Do. do.

7·5 per cent. Light grey, broken very irregularly, sound.

10 per cent. Light grey, fairly crystalline, irregular in texture, not quite sound.

Before leaving this part of the subject, it may be well to refer to what has been urged as an objection to the results brought forward in this paper, namely, that they are in most cases exceptionally high. This is illustrated in the following table:—

Tensile—	Author.	Woolwich, 1858.	Fairbairn, 1853.
Maximum ..	15·70 tons.	14·05 tons.	—
Minimum ..	4·75 „	4·85 „	—
Crushing—			
Maximum ..	92·54 „	58·42 „	95·9 tons.
Minimum ..	34·10 „	22·54 „	40·7 „
Specific gravity—			
Maximum ..	7·719 „	7·268 „	7·530 „
Minimum ..	6·924 „	6·886 „	6·771 „

In the second column are the results obtained at Woolwich in experiments conducted upon a large number of British irons, and published in the report "Cast Iron Experiments, 1858," p. 155. My attention was called to this report by Mr. John Spiller in June last, and I am obliged to him for introducing me to the most complete and interesting experiments on this subject with which I am acquainted. It is my intention shortly to refer to these results in a separate paper, when I hope to show that they furnish strong support of my own

observations. It is necessary to explain how it was that these important experiments were previously overlooked. It is true that they are quoted in various text-books, including *Watts' Dictionary* and Percy's "Iron and Steel." But in every case, so far as I am aware, the analyses and the mechanical tests were separately referred to, and, only recently being able to obtain access to the report itself, I had no reason to connect the mechanical tests recorded in one place with the chemical analyses published in another.

In considering the objection previously mentioned, however, it must be remembered that special care was taken in my experiments to prepare iron unusually free from the ordinary impurities, and that the carbon is always uniformly low for cast iron. Hence we should naturally expect the maximum results to be somewhat higher than usual. There would be more force in the objection if the results had been *lower* than usual, since then the tests might have been considered untrustworthy; in the present instance, however, such a supposition is evidently quite out of the question.

If now the various curves which have been given in this paper be examined the following conclusions may be drawn:—

1. That a suitable small addition of silicon to the cast iron previously almost entirely free from silicon is capable of producing a considerable improvement in the mechanical properties of the metal.

2. That the amounts of silicon capable of producing the maximum increase are probably as follows:—

For crushing strength	about 0·80 per cent.	
„ modulus of elasticity	„ 1 00	„
„ specific gravity (in mass) . . .	„ 1·00	„
„ tensile strength	„ 1·80	„
„ softness and working qualities	„ 2·50	„

3. That in cast iron where general strength is required the amount of silicon should not vary much from about 1·4 per cent.; but that when special softness and fluidity are required about 2·5 per cent. may be added. Even in the latter case, however, any increase beyond 3 per cent. must be dangerous.

In connection, however, with the above statements, it must be remembered that any considerable quantity of other elements, besides carbon and silicon, will materially affect the properties of the metal, and probably also the amount of silicon which should be present, in order to produce any desired character. The results are only strictly true under the circumstances of my experiments, and a careful comparison of the results of a large number of observations upon different kinds of iron will be necessary before the conclusions drawn may be

considered absolutely trustworthy. Upon this work, I am at present engaged.

At the Glasgow meeting of the Iron and Steel Institute in September last, an interesting paper was read by Mr. Charles Wood, in which it was shown that by a suitable addition of siliceous pig iron to Cleveland iron, castings of softer character could be obtained. Mr. Wood also showed that by adding silicon to white cast iron the metal passed gradually into soft grey iron with increased tenacity, thus confirming the results given in my previous paper. The addition of siliceous iron was carried on during several months' working, running 60 to 70 tons per day, and satisfactory results were obtained. Mr. Wood recommends that for castings where strength is required the silicon should be about 1·8 to 2·0 per cent., while for soft, sharp, clean castings about 2·6 to 3 per cent. of silicon is preferred. These numbers are in each case about $\frac{1}{2}$ per cent. higher than those deduced from my experiments, and the difference probably depends upon the phosphorus present in Cleveland iron.

Since my paper was written I have received the following note from Mr. Wood :—

"I am still using silicon pig largely in the foundry, and since reading my paper have sold several lots to different founders, who speak very favourably of the softening effect. I think myself, on further experiments, that my percentages are rather high. For strong iron 1·5 to 1·75 per cent. would be nearer, whilst 2·5 to 2·75 might be taken for softness, although 3·00 will do no harm, as in many classes of castings softness is of greater importance than a slight decrease of strength."

I may now perhaps be allowed to say a few words as to the cause of the changes which silicon produces when added to pure cast iron.

It has long been observed that certain kinds of grey iron, when quickly cooled, may be hardened, their specific gravity increased, and their character changed, from grey to white. On the other hand, certain white irons when strongly heated, and afterwards allowed to solidify slowly, become converted into grey iron, which, on account of its greater liquidity and softness, is preferred for many purposes. But it has been shown by Dr. Percy ("Iron and Steel," p. 117) that certain kinds of grey iron cannot be rendered white by chilling; and this fact is confirmed by Ledebur; on the other hand, Percy was unable to change some kinds of white iron into grey, even by a very high temperature and subsequent slow cooling (p. 121). Hence though in the majority of cases the question of white or grey iron may be settled by the circumstances of temperature and rate of cooling, yet in other instances it depends on chemical constitution, and the character of the metal can only be changed by altering the chemical

composition. Irons which are permanently white are rich in manganese or sulphur, but deficient in silicon, whilst irons that are permanently grey are probably rich in silicon and poor in manganese and sulphur. Thus No. 1 dark grey iron, which is highly graphitic and generally also rather highly siliceous, is found to be quite unsuitable for the production of chilled castings, whilst the iron which is found most suitable for this purpose is "strong," usually No. 4 or 5, and contains either a relatively small proportion of silicon, or a large proportion of manganese or sulphur. If we examine into the relationship between temperature and composition, we find that a high temperature, which is found to be necessary for the production of a graphitic iron, is also the most suitable for the reduction of silicon; whilst, on the other hand, the low temperature necessary for the production of white iron lowers the amount of silicon but favours the absorption of sulphur.* It would seem, therefore, that the character of the iron depends not on the temperature alone, but also on those chemical changes which accompany the alteration of temperature.

In this connection I have examined the composition of more than 180 specimens of pig iron, as shown by analysis, a few of which are original, but the great majority have been selected from the works of Percy, Abel, Lowthian Bell, and others. The lowest percentage of silicon found in a specimen of British grey pig iron is 0·81, whilst the highest percentage of silicon in any specimen of white iron, not containing an abnormal quantity of either sulphur or manganese, is under 1 per cent. It must be mentioned, however, that in the case of foreign irons this difference is not quite so plainly marked; and further, that analyses performed 30 years ago or upwards have been rejected, as possibly misleading; whilst some doubtful cases have also been omitted in which the analyses were more or less incomplete. It is not contended that the rule has no exceptions, but it is believed that the general fact has been proved, without the slightest doubt, in the case of British irons. Now, as no other constituent varies in the same manner as silicon has been shown to do, we are justified in concluding that the effect noticed is due, in great part, to a difference in the proportion of silicon present. It has even been stated, on the authority of Karsten and others, that in castings of grey iron the outer chilled portion contains more carbon and less silicon than the inner grey portions.

I do not contend that this explanation of the cause of the difference of the method of occurrence of carbon in cast iron is new. On the contrary, reference has already been made to the observation of Sefström, mentioned by Dr. Percy, "that the carbon in grey iron, in which much silicon exists, say from 2 to 3 per cent., is wholly or

* I. Lowthian Bell. "Iron and Steel," p. 416.

nearly so, in the graphitic state." And, 30 years ago, Messrs. Price and Nicholson at the works of the Lilleshall Iron Company, were producing iron by a patent process in which grey iron of good chemical quality was melted with the product of the finery forge in proportions regulated by the applications the product was to receive (No. 2618, November 20th, 1855).

In spite of these facts, and others of a similar kind, the close connection between the percentage of silicon and the mode of occurrence of carbon, did not appear to be understood. It is, however, very plainly seen in the two series of experiments conducted respectively by Mr. Wood and myself; although it must be borne in mind that our conclusions are only true when manganese and sulphur are present in but small quantity, and when also the circumstances of temperature and rate of cooling are as far as possible uniform in the different specimens examined.

These questions have been referred to at greater length on account of the interest attaching to the explanation of the results obtained in these experiments. Thus, at the Glasgow meeting of the Iron and Steel Institute, in September last, very considerable difference of opinion was manifested with regard to the question of the influence of silicon on the properties of cast iron. The opinion was expressed, and pretty generally endorsed, that "silicon or glazed pigs were always bad and unreliable, whatever they were mixed with," and that "as to silicon in pig iron itself the less that could be had the better." On the other hand, Mr. Stead agreed "that the less silicon they had in casting the better, provided that, practically, in the casting they kept the carbon in the graphitic condition." And he has kindly expressed his opinion for me as follows: "The strongest iron useful for general foundry purposes is that which contains sufficient silicon to prevent too large a proportion of the carbon remaining in the combined state in the iron when solidified."

I do not think there can be much doubt as to the truth of the result stated in the latter opinion of Mr. Stead, for not only does it agree with the deductions drawn from the experiments mentioned in the earlier part of this paper, but every practical man knows that the strongest iron is a close-grained grey, and one therefore which nearly approaches the limits of grey iron in the direction of mottled or white. But at the same time, in the present state of our knowledge, it appears unreasonable to attribute the whole effect to the action of silicon in rendering the carbon graphitic. What the action of silicon may be, when added to pure iron, in small but gradually increasing quantities, we do not know; and, after numerous attempts to solve this question, I must confess myself no further advanced than when I first began. It appears much more reasonable to suppose the results

we have noticed as the sum of two influences, namely, that of silicon upon iron itself, combined with its influence in the production of graphitic carbon, than to assume that the whole effect is "due to the latter cause alone. Hitherto we have no experimental evidence to support the view that "silicon is always bad" in its effects on cast iron. On the contrary, there is much evidence of an opposite nature, quite apart from that furnished by my own experiments, for it is notorious that "refined metal," which is of special chemical purity and contains only a few tenths per cent. of silicon, is quite unsuitable for foundry purposes, being deficient in tensile strength, too hard for working, and often unsound.

Further, although we find that, in the presence of silicon, a low percentage of combined carbon always accompanies a strong iron, we do not find that the strongest iron has the *lowest* combined carbon, as we should expect if the result were due merely to the separation of graphite. This is illustrated both in the analyses by Mr. Stead, and also in those I have previously given (this vol., p. 581). Again, on examining Fig. 5 (p. 908) it will be seen that the effect produced by the addition of silicon is regular and progressive. We find that up to 1 per cent. the improvement is quite obvious alike in crushing strength, modulus of elasticity, and tensile strength, though this improvement is *not* accompanied by the separation of graphite; between 1 and 2 per cent. we have the strongest iron, accompanied by much graphitic carbon; with upwards of 2 per cent. we have inferior iron, though the gradual deterioration in quality is not accompanied by any regular increase in combined carbon; on the other hand, this distinctly decreases in quantity as the metal becomes weaker. Or, to state the matter in another form, if the effect noticed is wholly due to the separation of graphite, then the percentages of graphite, if expressed in a curve, should be of the same general shape as those curves we have given in Fig. 5; as this is not the case, we are justified in concluding that the separation of graphite is but a part of the effect produced by silicon, and not the whole effect. It is therefore probable that the improvement in the mechanical properties of cast iron, produced by the addition of silicon, is owing partly to a direct beneficial effect due to suitable proportions of silicon itself, and partly to a secondary influence which silicon exerts on the carbon present.

In conclusion, it may be added that I hope shortly to be able to bring forward evidence based upon the researches of Fairbairn, Abel, and others, to support the conclusions I have already drawn, and to show how far the results given in this paper are confirmed, or modified, by the teaching derived from the study of a large number of independent and most carefully conducted experiments.

LXXXIV.—On the Relation of Diazobenzeneanilide to Amidoazobenzene.

By R. J. FRISWELL and A. G. GREEN.

IN the year 1862, Griess (*Annalen*, **121**, 257), who had four years previously given to the world the first of that remarkable series of researches on the "substitution of nitrogen for hydrogen in organic amido-compounds," which has since proved the parent of so many discoveries, first turned his attention to the study of his reaction upon organic bases.

The first compound discovered was that to which Griess gave the name of "diazoamidobenzol" (*loc. cit.*, 258),* and it was prepared by passing a stream of nitrous gas through aniline dissolved in from six to ten times its weight of alcohol in the cold.

In the following year the first azo-colouring matter made its appearance as a commercial article under the name of "*aniline yellow*," from the works of Messrs. Simpson, Maule, and Nicholson. It was prepared by a process devised by the late Mr. Frederic Field, F.R.S., which consisted in the passage of a stream of nitrous gas from nitric acid and arsenious oxide, through aniline or aniline dissolved in alcohol. The subsequent steps were the recovery of the alcohol and unaltered aniline by steam distillation, first alone and then with caustic soda, the solution of the base in alcohol, and its separation from tarry matters, and finally the conversion of the alcoholic solution of the base into the oxalate by the addition of oxalic acid.

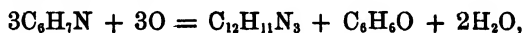
The constitution of this substance was, it need hardly be said, quite unknown, and its preparation was entirely empirical.

In 1866, Griess and Martius (*Zeit. Chem.*, 1866, N.S., 2, 132) published a paper in which the first amidoazo-compounds were described. They were aware of the fact that aniline yellow was prepared in some way by the action of nitrous gas upon aniline, and believed it to be identical with Griess's "diazoamidobenzol." Requiring a large quantity of the latter, they purchased aniline yellow and commenced to purify it, discovering directly that it was not diazobenzeneanilide, but that it was the oxalate of a base, the empirical formula of which was identical with that of diazobenzeneanilide. They showed that on reduction it split up into paraphenylenediamine and aniline, and accordingly gave it the constitutional formula $C_6H_5 \cdot N_2 \cdot C_6H_5 \cdot NH_2$, and called it "amidoazobenzol."

They also found that a colouring matter manufactured by Messrs.

* We propose throughout to call this body diazobenzeneanilide, following a suggestion in a note to § paper by A. Sarauw (*Ber.*, **14**, 2443).

J. J. Muller and Co., of Basle, by the action of stannate of soda upon nitrate of aniline in boiling solution consisted essentially of the same product, and as they found phenol to occur as a bye-product in both processes, they were led to believe that the action was on the whole an oxidising one as follows:—



and they decided that the production by the nitrous gas process was only a question of temperature, the one isomeride, diazobenzene-anilide, being produced in the cold, the other, amidoazobenzene, when the reaction took place in a warm solution (*loc. cit.*, 133).

In the same year Kekulé (*Zeit. Chem.*, 1866, N.F., 2, 688) showed that diazobenzeneaniline, if left in contact with a solution of an aniline salt, spontaneously changed into amidoazobenzene after an interval of two or three days; moreover he observed that the first effect of the action of nitrous gas on aniline in alcoholic solution was to produce diazobenzeneanilide, and he rightly accounted for the formation of phenol by ascribing it to the decomposition of that compound.

Kekulé suggested that the change from one isomeride to the other was in reality a case of double decomposition, and observes in the course of his paper that since one of the products of this change is aniline hydrochloride, a small quantity of an aniline salt ought theoretically to convert a very large quantity of the anilide.

In 1875, Baeyer and Jaeger (*Ber.*, 8, 151) prepared diazobenzene-ethylamide and diazobenzenedimethylamide, compounds analogous to diazobenzeneanilide, in which the second half of the molecule was the residue of ethyl- or dimethyl-amine. These compounds they treated in alcoholic solution with aniline hydrochloride, and found that in both cases amidoazobenzene was produced, while ethylamine and dimethylamine hydrochlorides appeared as the correlative products of the reaction, thus greatly strengthening Kekulé's double decomposition theory, which was also further confirmed by Nietzki's observation (*Ber.*, 10, 662) that paradiazotolueneparatoluide, reacting either with aniline or with orthotoluidine hydrochlorides, formed amidoazo-compounds with concurrent formation of paratoluidine hydrochloride. At this point the matter has been allowed to rest, the double decomposition theory being considered to comprehend all the facts.

In the course of some experiments undertaken with the object of obtaining amidoazobenzene directly, we have been led to question the validity of the received explanation of the cause of this isomeric change, for we think that the experiments we are about to describe throw considerable doubt upon it.

It will, we think, be readily conceded that if the received explanation is valid, there is no reason to suppose that amidoazobenzene could not under suitable conditions be formed directly by the combination of diazobenzene with aniline hydrochloride. Acting on this supposition, we have endeavoured to obtain this reaction, but although we have varied the conditions in every possible way, both as to temperature, acidity, concentration, solvent, order of mixture, and mass of reacting substances, we invariably found that diazobenzeneanilide was first produced.

Conditions of Formation of Diazobenzeneanilide.

Thus it is formed—

(a.) By the action of a molecular proportion of sodium nitrite on one of aniline hydrochloride and one of aniline at any temperature between 0° and 90° .

(b.) By the action of an alkaline solution of diazobenzene hydrate on aniline.

(c.) By the action of diazobenzene chloride on aniline at 0° to 10° .

(d.) By the action of diazobenzene chloride on aniline suspended in boiling water.

But if the product of the reactions *c* or *d* are left for a few hours in the solutions in which they are formed, they are slowly converted into amidoazobenzene chloride.

(e.) Sodium nitrite added to aniline in solution in excess of strong or dilute acetic acid produces diazobenzeneanilide.

(f.) Sodium nitrite in fine powder added to a solution of aniline in toluene with excess of acetic acid produces diazobenzeneanilide.

(g.) Sodium nitrite added to excess of aniline hydrochloride or of any mixture of aniline and aniline hydrochloride, no matter how great the mass, always produces diazobenzeneanilide.

It will thus be noticed that in every case this compound was produced as a first product, even when, as in cases *c*, *d*, *e*, and *g*, it was formed in the presence of excess of aniline hydrochloride or of an acid, although under such conditions a second reaction slowly takes place with the production of the isomeric compound.

We have shown that the change is in no way a function of temperature, acidity, or of the presence of aniline hydrochloride alone, since diazobenzeneanilide is formed first under all circumstances. It is extremely difficult to understand this transformation of a compound under conditions which are precisely the same as those which attend its production; indeed the phenomena appear to us more to resemble the birth and death of an organism than any other change with which we are acquainted among chemical substances. Since the

diazobenzeneanilide is formed in the presence of aniline hydrochloride, why should it, apparently by mere lapse of time, change into the isomeric substance? If the latter is (and it undoubtedly is) the more stable compound, why should it not form at once, and why does it only arise as a subsequent stage in the history of the transformation of a less stable compound?

Conditions of the Reacting Bodies during the Change.

Diazobenzeneanilide was prepared in the usual way, thoroughly washed with dilute acetic acid and then with water, dried, twice recrystallised from pure benzene, and then three times from alcohol; its m. p. was 96°. One molecular proportion (5 grams) of this was suspended in cold dilute hydrochloric acid containing 0.91 gram HCl (1 mol.). Under these conditions we found that in the course of from 12 to 15 hours it is converted into amidoazobenzene chloride mixed with tarry substances and phenol. The latter is due to the decomposition of diazobenzene chloride, for during the whole of the time we were able by appropriate treatment to prove the presence in solution of diazobenzene chloride and aniline hydrochloride. After extracting the solid product with toluene to remove tarry substances, pure amidoazobenzene chloride was left in steel-blue needles, the yield being 2.5 grams or 50 per cent. It thus appears that diazobenzeneanilide in the presence of hydrochloric acid is decomposed into diazobenzene and aniline hydrochloride, which then slowly reunite in a different way to form amidoazobenzene.

When excess of acid is employed, complete solution of diazobenzeneanilide ensues, the substance being resolved into diazobenzene and aniline chlorides, which are prevented from again uniting by the excess of hydrochloric acid, the neutralisation of which reprecipitates diazobenzeneanilide. If metaphenylenediamine is added before neutralisation diamidoazobenzene (chrysoïdine) is formed. The presence of aniline hydrochloride, ammonium chloride, or zinc chloride in the acid solution, does not appear to influence the change in any way whatever. The higher the temperature, the more rapid is the change, and the greater the proportion of tarry decomposition products.

The experiment was carefully tried on a very considerable scale, as much as 2 or 3 kilos. of diazobenzeneanilide being employed. The substitution of acetic for hydrochloric acid retarded the action, and gave rise to increased decomposition. Zinc chloride and ammonium chloride solutions produced no change. A molecular proportion of nitric acid acted in almost the same way as hydrochloric acid,

whilst half or even one molecular proportion of sulphuric or oxalic acid diluted produced scarcely any change.

The latter fact appears to be opposed to the theory that might be advanced, that the presence of an acid tends to induce the formation of a base to combine with it, since we should expect that this tendency would be increased by using strong acids, such as sulphuric and oxalic acid, instead of hydrochloric acid.

In alcoholic solution, the conversion of diazobenzeneanilide into its isomeride is, as is well known, caused in the cold by aniline hydrochloride. We have found that the same result is produced by the action under like conditions of zinc chloride, and more slowly and on heating by calcium chloride.

During all these reactions, whether in alcoholic or aqueous solution, some evolution of nitrogen always occurs, some of the anilide or rather the diazobenzene produced by its resolution being converted into phenol and tarry substances.

It thus appears that diazobenzeneanilide is capable of being converted into its isomeride by treatment with one equivalent of an acid, such as hydrochloric acid, or of any unstable salt capable of furnishing the acid required, such as aniline hydrochloride, zinc chloride, calcium chloride, &c. Hence we consider the double decomposition theory proposed by Kekulé, and considered to have been proved by the researches of Baeyer and Jaeger and of Nietzki, as untenable; the conversion of the diazobenzeneanilide into amidoazobenzene in the ordinary manner by treatment with aniline hydrochloride dissolved in aniline is, as we consider, entirely due to the hydrochloric acid present, and has nothing to do with the aniline, which merely serves as a convenient solvent, and by its presence prevents the decomposition of the diazobenzene, which is formed as an intermediate product by the resolution of the diazobenzeneanilide previously to its recombination in a different manner to form the isomeride. The formation of amidoazobenzene, by treating diazobenzene-ethylamide and diazobenzenedimethylamide with aniline hydrochloride, can be easily explained in a similar way; the hydrochloric acid first resolves them into diazobenzene and ethylamine or dimethylamine, and the diazobenzene then combines with the aniline present to form amidoazobenzene. The same remark applies also to Nietzki's observations on the actions of aniline and orthotoluidine hydrochloride on paradiazo-tolueneparatoluide.

From the above experiments, it would appear that diazobenzeneanilide, under the influence of hydrochloric acid or of an unstable chloride, is resolved into its constituents, and that the diazobenzene thus produced is capable of *slowly* recombining with aniline hydrochloride to form amidoazobenzene hydrochloride, although if the

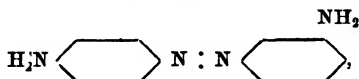
union is compelled to take place *quickly* by neutralising the acid, the anilide is reformed.

It would thus seem that the conclusion that *time* is required for the rearrangement of the molecule is irresistible. If the temperature is raised, the time required for the reaction is greatly diminished (though we have never succeeded, at any temperature, in getting an instantaneous reaction in this direction), but, on the other hand, the amount of destructive decomposition is greatly increased. Beyond the fact of the necessity of this time interval, we cannot offer any further explanation of this most remarkable reaction or rather chain of reactions.

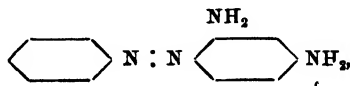
The fact that diazobenzeneanilide is formed by the direct combination of diazobenzene chloride and aniline, and that the product, when left in the solution in which it was formed under exactly the same conditions under which it was formed, by mere lapse of time apparently is again resolved into its constituents, and that these constituents again unite, but in a different manner, to form amidoazobenzene hydrochloride, is to us, at present, perfectly inexplicable, and we consider that it stands quite apart from the generality of chemical changes. If the diazobenzeneanilide is destined to be again resolved into its constituents, why should it be formed? And if diazobenzene chloride can combine with aniline to form amidoazobenzene, why does it not do so in the first place?

It has been suggested by Baeyer and Caro (*Ber.*, 7, 966) that diazobenzene can slowly change into the isomeric compound nitrosoaniline, $C_6H_4(\overset{1}{NO})\cdot\overset{4}{NH_2}$, and that it is by combination of the latter with aniline that amidoazobenzene is produced. If this theory were correct, it would certainly help to explain the mystery, but it is open to the objection that it would make the formation of amidoazobenzene take place in quite a different way from that of di- and tri-amidoazobenzene and all other azo-compounds that are formed directly, or else necessitate the alteration of the received constitution of these compounds.

For instance, by the action of nitrosoaniline on metaphenylenediamine, the symmetrical diamidoazobenzene,



would be produced, whereas chrysoïdine undoubtedly has the unsymmetrical formula



for on reduction, it yields aniline and 1 : 2 : 4 triamidobenzene ; whereas the first compound would yield paraphenylenediamine and metaphenylenediamine in equal molecular proportions.

The resolution of diazobenzeneanilide into diazobenzene and aniline explains many facts which have been observed by Griess and others. Thus it was by the action of bromine upon diazobenzeneanilide that Griess in one of his earlier papers (*Proc. Roy. Soc.*, **13**, 376) prepared diazobenzene as the bromide, tribromaniline being formed as the correlative product. The reaction no doubt consisted in the resolution of the anilide into diazobenzene and aniline, the latter being further attacked by the excess of bromine and thus removed.

Again, Griess (*Proc. Roy. Soc.*, **12**, 418) first obtained diazobenzene nitrate by treating diazobenzeneanilide with nitric acid containing nitrous acid, in which case the nitric acid would resolve the anilide into diazobenzene nitrate and aniline nitrate ; the latter would then be attacked by the nitrous acid and also be converted into diazobenzene nitrate.

The formation of phenol during the preparation of amidoazobenzene by various processes, and by the decomposition of diazobenzene anilide by acids, has been repeatedly observed, and its source is now clear.

Formation of Diamidoazobenzene and Homologues from Diazobenzeneanilide.

20 grams (1 mol.) of pure diazobenzeneanilide was warmed for several hours with an aqueous solution of 16 grams (1 mol.) metatolylenediamine hydrochloride. On boiling the mixture, aniline and water distilled over, and the solution contained the hydrochloride of diamidotolueneazobenzene (tolylenediaminechrysoidine) ; it was filtered, and on cooling the chrysoidine crystallised out. The yield was 24 grams, or 96 per cent. of the theoretical quantity. The reaction takes place in exactly the same way with metaphenylenediamine, and also occurs, though much less perfectly, at the ordinary temperature. The tolylenediamine was employed, as it can be very readily obtained in a pure state.

We consider the mechanism of this reaction to be exactly the same as with those previously described, the diazobenzeneanilide being first resolved by the acid and the diazobenzene formed combining with the diamine.

Resolution of Azoxybenzene.

Wallach and Belli (*Ber.*, **13**, 525) have found that azoxybenzene, by treatment with sulphuric acid, is converted into the isomeric compound oxyazobenzene. It appears to us extremely probable that this

pulverulent substance may be obtained. Like other similar products, however, the yellow substance can be separated into a white one and a very small quantity of a yellow one not yet examined. The white or yellow substance is a hydrocarbon, distinct apparently from any yet described.

The purified hydrocarbon is amorphous in appearance, but when deposited from a benzene solution forms minute crystals. From acetic acid, it is more distinctly crystalline, and on drying is of a whiter colour and silky lustre. It is denser than carbon bisulphide, highly electric when dry, and when prepared in the way adopted, has a bright yellow colour. This colour, however, as mentioned above, is due to a matter adhering in minute quantity to the main product; the latter may be deprived of colour, more or less completely, by cooling its hot solution in benzene or acetic acid after it has been exposed for some time to the sun. The yellow colouring matter in solution is thereby changed, but only slowly, into an orange-red and still soluble matter, and in this respect differs from the chrysogen of coal-tar which is bleached by the sun.

Both the yellow and the white modification of the hydrocarbon can be sublimed almost unchanged in a vacuum, but with difficulty. When heated in the air, it darkens and is partly decomposed, apparently by oxidation. Its melting point is accordingly not sharply defined, and lies between 280° and 285° .

There is no good solvent for the hydrocarbon. Boiling heavy benzene dissolves about 2 per cent., and carbon bisulphide, ether, chloroform, glacial acetic acid, light petroleum, and alcohol also dissolve more or less.

When a cold ethereal solution of the yellow form of the hydrocarbon is poured on to a filter-paper, the edges and upper part of the filter soon throw out, in consequence of the evaporation of the ether, a crystalline arborescence, several millimetres high, which is of a pure white colour. Shortly after its formation, the spicules of this arborescence suddenly shrink up, one by one, and resume the original bright yellow colour. This series of phenomena is very striking.

Cold sulphuric acid gradually changes it to a bright brown flocculent substance, probably a quinone. Moderately heated, it dissolves in the acid to a fine deep chromium-green coloured liquid, which becomes indigo-blue when more strongly heated. Poured into water, neither the green nor the blue solution deposits any insoluble matter.

In hot glacial acetic acid, chromium trioxide readily forms a flocculent orange-red quinone, readily converted to a colourless soluble substance by the further action of the chromium trioxide. The quinone is brown when dried, and is but little soluble in benzene, chloroform, or alcohol.

Nitric acid acts slightly on the hydrocarbon, converting it apparently to its quinone, or to a nitroquinone, very little soluble in the acid.

Picric acid forms a reddish-brown, slightly crystalline compound with the hydrocarbon, which is decomposed by washing with alcohol or with water.

Bromine acts moderately on the hydrocarbon, evolving hydrobromic acid and yielding a bromine-derivative of the hydrocarbon, soluble both in chloroform and benzene. It is a brown substance, not yet obtained in the crystalline state.

Both yellow and white forms of the hydrocarbon have been burnt for analysis, with results which correspond to those calculated for $n\text{C}_4\text{H}_8$, where n is perhaps 6:—

	Yellow.			White.		C_4H_8 .
	I.	II.	III.	IV.	V.	
Carbon . . .	94.10	94.08	94.15	94.13	94.10	94.12
Hydrogen..	5.99	5.98	5.88	6.10	6.08	5.88
						<hr/> 100.00

The hydrocarbon, "petrocene," which Hemilian obtained in 1877 from Pennsylvanian petroleum, is not only like ours in origin, but also in several of its properties. It melts, however, above 300° , is almost insoluble in ether, and the formula assigned to it is $\text{C}_{32}\text{H}_{22}$.*

Prunier and David's hydrocarbons, which in 1877 had been exhibited as petrocene, scarcely need any consideration. One of the hydrocarbons which Sadtler and McCarter examined in 1881 agrees with ours in melting point, but differs in composition, having the formula $\text{C}_{16}\text{H}_{14}$ = carbon 93.2 per cent. Picene somewhat resembles our hydrocarbon, but differs in its melting point (330 — 335°); in being capable of distillation in absence of oxygen; in its distinct crystalline form; its solubility in many solvents being less; solubility of its quinone in chloroform, &c.; and in its crystalline and insoluble bromine-derivative. Benzerythrene, described by Schultz, is somewhat like our hydrocarbon, but melts at 307 — 308° , and is soluble in cold nitric acid. Others are too remote from ours in properties to require consideration.

We hope to be able to extend our examination of this hydrocarbon from Japanese petroleum, and to give a more precise account of its properties than in this preliminary notice.

* $\text{C}_{32}\text{H}_{22}$ has 0.46 more carbon and 0.46 less hydrogen than C_4H_8 .

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Page	Line	
91	12 from top,	for " $C_{20}H_{24}O_4$ " read " $C_{20}H_{24}O_4$ "
193	18 " "	" "3244" read "3244."
208	16 " "	" "to" read "at."
"	6 " bottom,	" "of sulphite" read "of sulphate."
212	14 " top,	" "sulphates" read "sulphonates."
216	7 " bottom,	" $\begin{array}{c} O \\ \diagup \quad \diagdown \\ Ca-SO_2 \end{array}$ read $\begin{array}{c} O \\ \diagup \quad \diagdown \\ Ca-SO_2 \end{array}$ "
217	4 " "	" "chloride" read "chlorine."
"	7 " "	" " $-S\triangleleft$ " read " $-S\triangleleft O$."
219	11 " top,	transpose " <i>Action of Sulphur Dioxide on Sulphites</i> (this vol., p. 209) to bottom of foot-note.
"	9 " bottom,	for " $2OSnCl$ " read " $2OSnCl_2$."
"	10 " "	" " $SnCl_2$ " read " $SSnCl_2$."
220	3 " top,	" " $O_2 \triangleright S \triangleright O_2$ " read " $O_2 \triangleright S \triangleleft O_2$."
221	23 " "	" " $-S-$ " read " $-S-$."
On page 226, line 5 from bottom, and on page 227, line 17 from bottom, the author wishes the word "carbonylamine" to be changed to carbonylamine, and the footnote relating to them to be cancelled.		
225	15 from top,	for "thionities" read "thionites."
228	11 " bottom,	" "Lössen" read "Lössen."
229	4 " top,	the sentence in italics to be read as a paragraph of the text in italics, not as a sectional heading.
"	18 " "	for "diazoammonium" read "diazo."
"	" " "	" "diazotammonium" " "azotammonium."
"	4 " bottom,	" "nitrites" read "sulphites."
230	14 " "	" "Exuer" " "Exner."
234	2 " top,	" "nitrites" " "nitrite."
256	19 " "	" "phosphorous" read "phosphorus."
363	15 " "	" " $\begin{array}{c} K \\ \diagup \quad \diagdown \\ KO-Sn \end{array}$ " " " $\begin{array}{c} K \\ \diagup \quad \diagdown \\ KO-SnO \end{array}$."
440	5 " "	" "last" read "test."
479	19 " "	" "Schmidau" read "Shimidzu."
534	8 " "	" "water" read "alcohol."
568	" " bottom,	" "necessarily" read "successively."
606	6 " "	" "conversion" read "convection."
624	5 " "	" "hydroxylamine" read "stannous chloride."
"	7 " "	" "stannous chloride" read "nitric oxide."
632	4 " top,	after "escaped" insert "the tube was sealed again and left for about 18 hours."
635	7 " "	for "nitrate" read "nitrite."
636	19 " "	" "sulphide" read "sulphite."

I. A. R. I. 75.

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